

4.0 ENVIRONMENTAL FATE AND TRANSPORT, TRENDS AND IMPACTS

4.1 Overview of Pesticide Transportation Vectors (Environmental Loadings) to the Great Lakes

As discussed in Section 3, there are many sources of Level I pesticides to the Great Lakes ecosystem. Before U.S. product cancellation, these pesticides were widely used by farmers, exterminators, public and private institutions, and the general public. While general information is available on the registered uses and quantities of Level I pesticides manufactured in the United States for a given year (refer to Section 3.0), there are limited data on actual product use at the state, county, or watershed level. This circumstance arose for two primary reasons: (1) for many years pesticide laws and regulations did not require detailed record keeping, and (2) for most of their registration periods, the products were not considered to present undue environmental risk.

Complicating an evaluation of Level I pesticides in the Great Lakes is the fact that some of the canceled pesticides are still being used in other countries. In those countries where they are no longer being used, cancellation and/or use-reduction frequently occurred after product cancellation in the United States. Because of the environmental persistence and atmospheric transport of Level I pesticides, the Great Lakes continue to receive “loadings” from these non-U.S. releases. Correspondingly, environmental persistence also allows the pesticides, as well as some degradation products, to move among terrestrial, aquatic, and atmospheric compartments within the Great Lakes basin.

Despite the lack of product-use information on Level I pesticides in the Great Lakes basin, information is available on:

- Properties and environmental behavior of Level I pesticides and like compounds; and
- Concentrations of Level I pesticides in air, water, soils, sediments, and tissues in and around the Great Lakes.

From the available information, it is possible to evaluate the current reservoirs of Level I pesticides and their degradation products (some of which also cause detrimental/unacceptable effects) in the environment. The primary means by which Level I pesticide effects and risks are described and understood are (1) measurement of pesticide concentrations in the field, and (2) evaluation of movement among the environmental compartments.

The transport and fate of Level I pesticides (and other chlorinated compounds) in the Great Lakes basin (and elsewhere) are generally a function of five main processes.

1. Ongoing, diffuse movement of legally applied products among environmental compartments (e.g., volatilization from soils);
2. Small and localized releases of improperly stored or illegally used old stocks;

3. Accidental releases from pesticide disposal or spill sites;
4. Product transformation (e.g. degradation); and
5. Burial in sediment.

The schematic in Figure 4-1 summarizes the major pathways and sinks of Level I pesticides in the Great Lakes basin. From an ecological and human-health perspective, pesticides are of concern only when the compounds are exposed to organisms and present a risk of detrimental or unexpected impact. Impacts can occur only if (1) the animal or human receptor is in the pathway of the pesticide, and (2) the exposure concentration is high enough to elicit an effect. Thus, the basis of concern about Level I pesticides is persistence in the environmental compartments in which there are organisms.

Pesticide persistence is reduced by either chemical or biological transformation processes or environmental sequestration. Sequestration of pesticides usually means natural burial in soils or sediments, where the compounds are tightly bound to organic carbon structures and there is little biological activity. Transformation processes, on the other hand, are variable and complex. A pesticide molecule that undergoes physical, chemical, or biological transformation in one environmental compartment might continue to be transformed/degraded in the same (or another) compartment by same or different processes.

Level I pesticides are subject to three major transformation processes: biodegradation, abiotic oxidation and hydrolysis, and photolysis. The rate of these processes depends on environmental conditions such as temperature, oxygen content, and vapor pressure, as well as the chemical structure and properties of the substance (e.g., water solubility) and the distribution of the pesticides in the various compartments of the environment. However, while sufficient exposure to transformation processes will eventually transform all Level I pesticides to benign constituents, as a group, Level I pesticides are very resistant to transformation (i.e., they have long environmental persistence).

The following discusses the general attributes of the five major types of environmental compartments of the Great Lakes that also serve as pathways of exposure: the atmosphere, surface and ground waters, soil and sediment, biota, and hazardous waste sites (i.e., “hot spots”). Of these five compartments, the atmosphere is the most dynamic; now that regional application of Level I pesticides has stopped it is also the most important to pesticide cycling and exposure in the Great Lakes basin.

4.1.1 Atmospheric Transport and Flux

Atmospheric deposition refers to the removal of pollutants (following transport) from the air to soil, water, and other surfaces. Deposition may occur directly to the water surface and/or indirectly to the land surface in the watershed, with subsequent runoff from rainfall carrying contaminants to the water body. Both local and distant sources can contribute to the

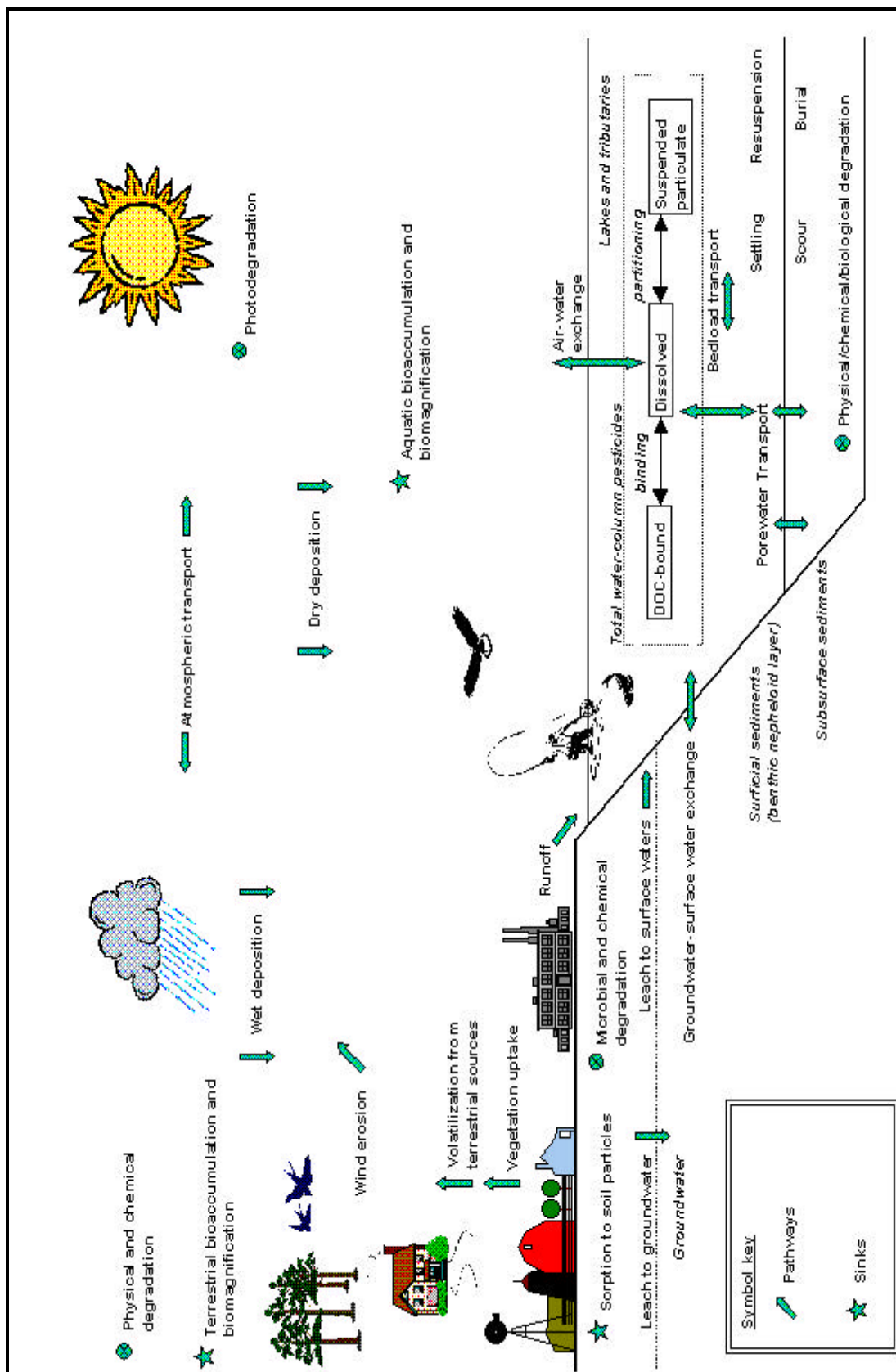


Figure 4-1. Pesticide Environmental Transports and Sinks.

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atmospheric transport and deposition of pesticides has been documented by numerous researchers, and is now believed to contribute significantly to contaminant inputs in surface waters such as the Great Lakes. Figure 4-2 shows the scale of the 1-, 3- and 5-day airshed for the Great Lakes compared to the lakes' watershed. Figures 4-3 and 4-4 from IADN (1998a) show back air-trajectory analyses for toxaphene and p,p'DDT, and demonstrate that airborne pesticides have the potential for long-range transport to and from the Great Lakes.

Major processes of atmospheric deposition to natural water bodies such as the Great lakes include: wet deposition, dry deposition, and gas exchange across the air-water interface (refer to Figure 4-1). Eisenreich et al., 1997 (reported in USEPA, 1997d) report that gaseous exchange of organic compounds at the air-water interface is an important phenomenon in the balance of pollutants occurring in air and water. Before cancellation of the Level I pesticides and use reductions of other organochlorine chemicals, the relatively high pollutant concentrations in the atmosphere caused net absorption of pesticides to the lakes at the water surfaces. At present, however, for some pesticides (IADN, 1998a; Hillery et al., 1998) the Lakes are now a source to the atmosphere.

4.1.2 Surface Water and Sediment

Surface Water. While in the water column, Level I pesticides are in one of three phases: bound to dissolved organic carbon, dissolved in the water, or bound to suspended particulates (refer to Figure 4-1). Because Level I pesticides are very hydrophobic (Log K_{ow} s of 2.5-7.4) water column pesticides tend to be bound to suspended sediment that is moving between land sources and lake sediments. Depending on amount of suspended particles in the water column, the temperature and other physical parameters, the dissolved pesticides are a significant component of the total water-column concentration. In addition, dissolved pesticides can change between the water and air compartments. The bidirectional air-water exchange of Level I pesticides means that the Great Lakes can be both a source and a sink for pesticides in the atmosphere.

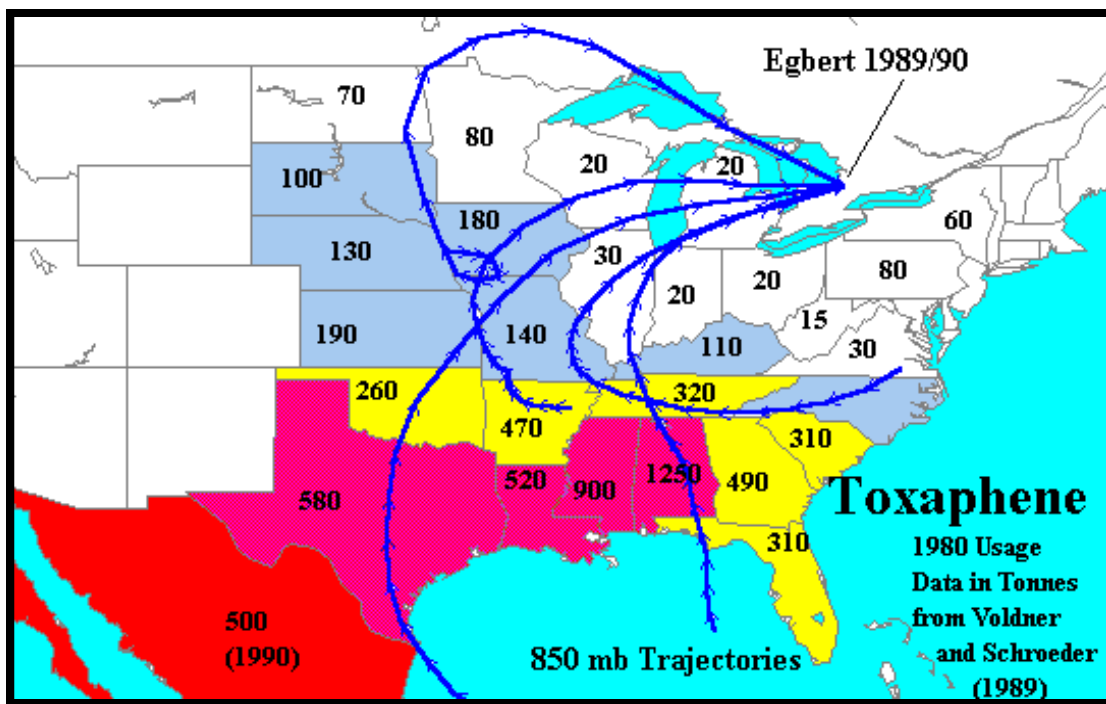


Figure 4-3. Toxaphene Use Distribution (in metric tons) and Back Trajectories at 850 mb Showing Potential Sources of Toxaphene to the IADN Satellite Site at Egbert, Ontario. The Trajectories Correspond to the Five Highest Concentrations.

Source: IADN, 1998a.

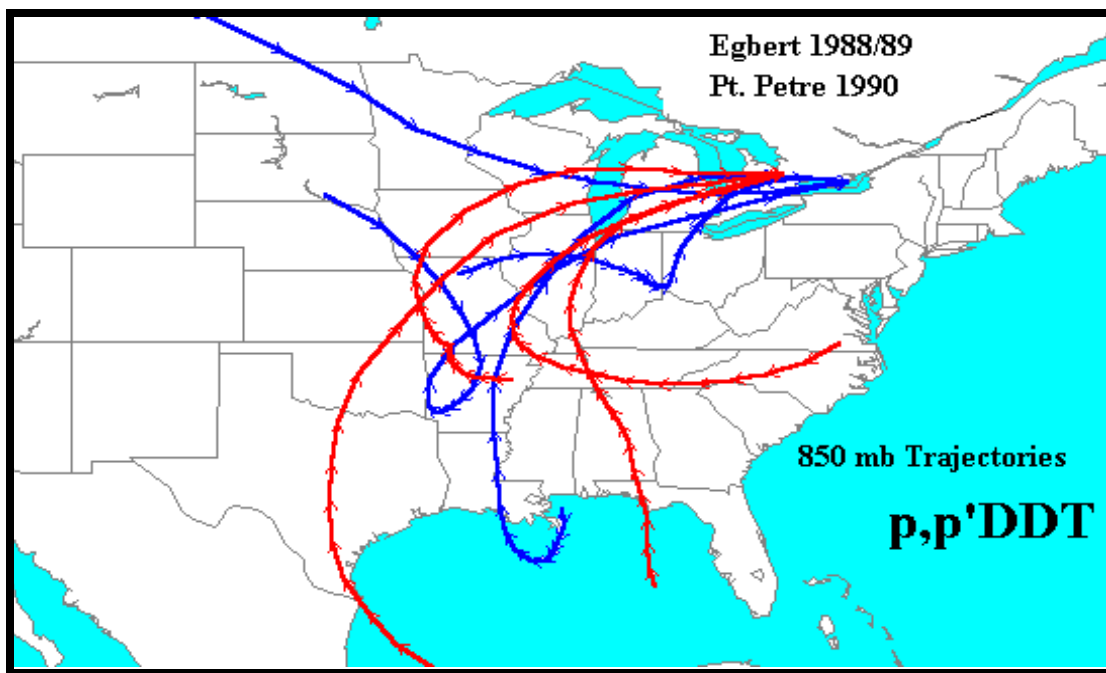


Figure 4-4. Back Trajectories at 850 mb Showing Potential Sources of p,p'-DDT to IADN Sites at Egbert and Point Petre, Ontario.

Source: IADN, 1998a

cides can also become components of sediment porewater. Porewater pesticides are not bound to particulate matter, and while movement along a particular pathway is small relative to the movement of particulate-bound pesticides, it can be an important exposure pathway to benthic organisms.

Sediment. Due to the hydrophobic nature of the Level I pesticides, transport and fate of these pesticides in the water column and sediments are closely linked to the movement and fate of particulate matter. As in other open water systems, particulate matter in the Great Lakes is either suspended in the water column or deposited on the lake bottoms in the sediments. Sources of particulate matter to the water column are both land runoff from Lake shores and tributaries and resuspension of previously deposited bottom sediments. Because particulate transport is a major determinant in Level I pesticide transport, water-column pesticides eventually become buried in the subsurface sediment layers of the Lakes. The deep subsurface sediments of the Lakes are long-term (geologic scale) sequestration sites for the pesticides, and are thus an environmental sink, isolated from most biological, chemical, and physical transformation processes.

Dated sediment cores have the potential for providing detailed chronologies and inventories of hydrophobic organic contaminant (HOC) input as long as the sedimentation process was not disturbed and mixing in the surface sediment is minimal.

4.1.3 Soil and Groundwater

Soil. Soil and groundwater pathways of Level I pesticides are short and slow relative to pathways in the air and water column. The main reason for this is the same as for pesticide movement in sediments—the compounds have a strong affinity for organic carbon and bind to soil particles. If the soil-associated pesticides stay on the surface, the compounds are more readily exposed to sunlight and other transformation processes. However, if the soil is covered (e.g., by mechanical tilling or vegetation overgrowth) the pesticides can persist for long periods. Surface soils, like the sediment surface layers, are also sites for transformation by microbes. In general, microbial activity decreases with increasing soil depth.

Groundwater. In the Great Lakes, lake water and ground water exchange, and associated dissolved fractions of Level I pesticides is not considered significant. There is no known research on this transport pathway for organic pollutants in the Great Lakes. While most Level I pesticides will be strongly sorbed to soil particles, as described for the aquatic environment, some of the pesticides will be in dissolved form and have the potential to leach into the groundwater. The pathway to groundwater, as well as the associated pathways of groundwater leaching to surface waters and groundwater-surface water exchange are considered to be exceedingly small based on the slow movement of groundwater, the pesticides' strong affinity for binding, and the lack of data demonstrating otherwise. Nevertheless, in certain locations of low organic-carbon sediments and high concentration of pesticides (e.g., at a spill site) the groundwater pathways could be important exposure vectors to resident biota.

4.1.4 Biota

Due to their persistence in the environment, and propensity to bioaccumulate, the Level I pesticides are still present in the tissues of fish, birds, and terrestrial animals, decades after cancellation. Contaminant concentrations in fish from the Great Lakes have been monitored for over 20 years. These programs were implemented to assess effects of contaminants to fish and on fish consumers, both human and wildlife. Although bioaccumulation in and of itself is not necessarily an impact, it is often used as an indicator of unacceptable or deleterious biological effects in animals, including human beings.

Historically, the primary human exposure pathways for these chemicals were associated with the consumption of agricultural products contaminated via pesticide applications. The ingestion of dairy products continues to be a significant exposure route. In Ritter et al. (IPC POPS Rept., 1995) it is reported that dieldrin is the second most commonly detected pesticide in pasturized milk, and that “milk, butter, and animal meats were primary sources if exposure” to human beings. However, with cancellation of Level I pesticide uses in the United States, potential exposures associated with consumption of vegetables and other agricultural products have been significantly reduced. In contrast, consumption of fish has become a primary route of exposure for humans and fish-eating (i.e., piscivorous) wildlife. Fish and aquatic invertebrates are readily exposed to the pesticides cycling through the environmental compartments of the Great Lakes, specifically through dissolved and suspended pesticides, as well as contaminated sediments. The food chain of the Lakes serves to magnify the pesticide concentrations in the organism, with large carnivorous fish having substantially higher concentrations of pesticides in their tissues than small fish or invertebrates that feed lower on the food chain. Correspondingly, piscivorous birds, minks, and some human subpopulations (e.g., subsistence fishermen) are exposed to very high doses of pesticides through their diet.

4.1.5 Hazardous Waste Sites

Since the cancellation of production and use of the Level I pesticides, direct discharges to the environment have greatly diminished. However, hazardous waste sites with elevated levels of these pesticides continue to serve as potential, ongoing sources to the Great Lakes watershed either through leaching into groundwater, soil runoff and erosion, or atmospheric transport. Therefore, it is important to consider the number and location of hazardous waste sites at which these chemicals have been detected, as well as the media in which they are reported.

National Priorities List (NPL). Table 4-1 lists the number of hazardous waste sites on the National Priorities List (NPL) at which Level I pesticides have been identified in one or more media as of May 1998 (Jensen, 1998). The NPL includes the most serious hazardous waste sites in the United States as identified by the Environmental Protection Agency for long-term federal cleanup activities (USDHHS, 1993). In general, these chemicals have been reported predominantly in either soil or groundwater, although several sites list sediment and surface water contamination as well. Table 4-2 provides a list of

the number of sites associated with each of the states in the Great Lakes Region. When evaluating the data presented, it is important to note that due to the ongoing addition and removal of sites from the list, the exact number of sites listed for a particular chemical may vary from year to year. Approximately 30% of the sites listing the pesticides as contaminants occur within the Great Lakes Region (Tables 4-1, 4-2). Of the current sites listing DDT as a contaminant, 44 are located in the Great Lakes Region, with 17 in New York alone (Table 4-2).

Table 4-1. Summary of NPL Sites Nationwide with Level I Pesticide Contamination^a

Chemical	Soil	Sediment	Surface Water	Groundwater	Total
Aldrin	47	15	7	34	69
Dieldrin	75	24	13	46	101
Chlordane	62	24	10	40	88
DDT	122	35	23	59	148
Mirex	1	2	1	3	3
Toxaphene	9	1	0	5	11

^a Sites may have more than one chemical, and chemicals may be present in multiple media.

Table 4-2. Summary of Hazardous Waste Sites in the Great Lakes Region with Level I Pesticide Contamination^a

Chemical	Illinois	Indiana	Michigan	Minnesota	New York	Ohio	Pennsylvania	Wisconsin	Total
Aldrin	0	2	2	0	7	3	3	3	20
Dieldrin	1	2	7	1	7	5	3	3	29
Chlordane	1	1	4	1	9	3	4	0	23
DDT	0	3	8	0	17	2	7	7	44
Mirex	0	0	0	0	2	0	1	0	3
Toxaphene	0	0	0	0	0	0	0	0	0

^a Sites may have more than one chemical, and chemicals may be present in multiple media.

Review of these data indicates that the presence of the Level I pesticides is relatively common throughout the United States. However, the extent to which these sites may impact the environment depends on the level of pesticide contamination present. While, for the most part, the presence of these compounds is incidental due to past legal uses and the ubiquitous nature of these compounds throughout the environment, there are some sites with heavy contamination of one or more of the Level I pesticides. For example, DDT has been detected in soils, groundwater, sediments and fish at the former Velsicol Chemical Corporation's Pine River NPL site in St. Louis, MI (USEPA, 1997a). The site was a former DDT manufacturing facility prior to the ban on DDT production. As recently as 1997,

maximum concentrations of total DDT (sum of DDT and metabolites) in sediment from the Pine River were as high as 32,600 ppm while average concentrations in carp in the vicinity of the site ranged from 49.70 to 58.07 ppm (Pers. Com., D. Macarus). Note that these fish concentrations were based on analysis of whole fish. Average total DDT concentrations in carp fillets from the St. Louis impoundment and below the St. Louis dam were 34.5 and 26.8 ppm, respectively. Activities are underway to control contamination and begin clean-up of the area (Bredin, 1999). Lake Sandy Jo (EPA, 1997b) in Gary, Indiana has been reported to have DDT in sediments, soils, surface water, sediments and groundwater (EPA, 1997b). Chlordane has been found in the sediments and soils of the Midco I Site, located within the aquifer for the Calumet (EPA, 1997c). Aldrin has been identified in leachate from the Love Canal industrial landfill in Niagara Falls, NY (USDHHS, 1993).

Mirex manufacturing facilities were primarily located near Niagara Falls, NY and State College, PA (USDHHS, 1995), likely accounting for the limited distribution of hazardous waste sites associated with this chemical. Between 1957 and 1976 the Hooker Chemical and Plastics Corporation in Niagara Falls, NY released mirex at rates of up to 200 kg/yr (USDHHS, 1995). The repository for wastes from this site, the 102 Street Landfill along the Niagara River is currently listed on the NPL (EPA, 1998b), though recent activities have resulted in containment of the contaminants and clean-up operations are underway.

Great Lakes Areas of Concern (AOCs). In addition to specific hazardous waste sites, the Great Lakes Program has identified forty-six highly polluted Areas of Concern (AOCs) within the Great Lakes that serve as both sinks and sources of contamination to the rest of the region (Figure 4-5; EPA, 1998b). Table 4-3 presents a summary of the AOCs that list pesticides as primary contaminants. In general, the majority of the AOCs associated with the Level I pesticides appear to be located in New York. For example, the Buffalo River, Niagara River, Oswego Lake, Rochester Embayment, and St. Lawrence River AOCs all have at least one of the Level I pesticides as a primary contaminant of concern (EPA, 1998c). In Ohio, elevated levels of DDT have been found in fish from the Black River and in sediments from the Cuyahoga River (EPA, 1998c). In Wisconsin, pesticides have been identified as chemicals of concern in the Milwaukee Estuary AOC (EPA, 1998c).



Figure 4-5. Designated Areas of Concern (AOCs) in the Great Lakes.

Source: Environment Canada, 1999

Table 4-3. Areas of Concern (AOCs) Listing Pesticides as Chemicals of Concern.

State	AOC	Chemicals
Illinois	None	NA
Indiana	None	NA
Minnesota	None	NA
Michigan	None	NA
New York	Buffalo River	Chlordane, DDT
	Niagara River	Mirex, Chlordane, DDT, DDE, dieldrin
	Oswego Lake	Mirex
	Rochester Embayment	Mirex, DDT, Chlordane
	St. Lawrence River/Massena	Mirex, DDT
Ohio	Black River	DDT
	Cuyahoga River	DDT
Pennsylvania	None	NA
Wisconsin	Menominee River	Pesticides
	Milwaukee Estuary	Pesticides

4.2 Documented Effects, Transport, Fate and Trends of Level I Pesticides in the Great Lakes

This section summarizes the documented findings to date related to the presence of Level I pesticides in the Great Lakes. Current and historical sources of pesticides to the Great Lakes Region are summarized and chemical-specific fate and transport issues are discussed. In addition, measured concentrations of the pesticides are presented by environmental compartment and evaluated with respect to temporal and spatial trends. The quality and quantity of the available data are limited, varying widely by matrix and location. As a result, it is difficult to draw definitive conclusions with regard to certain trends. The implications of the various concentration and trend data are discussed in the following section (Section 4.3).

4.2.1 Aldrin and Dieldrin

As discussed in Section 3.1, aldrin and dieldrin are insecticides that were manufactured in the United States until 1974. The primary use was for control of agricultural pests through application to the soil, and for subterranean termite control.

4.2.1.1 Sources of Aldrin and Dieldrin

There are currently no known direct releases of aldrin and dieldrin to the environment as the result of manufacture. As previously discussed, neither chemical has been produced in the United States since 1974, and recent Toxic Release Inventory (TRI) records indicate no reportable releases to the

environment since 1988 (USDHHS, 1993). As a result, the primary source of aldrin and dieldrin to the environment has been past agricultural use and application for termite control. Although application of these compounds was canceled in the 1970s, historical applications resulted in persisting soil residues which continue to serve as sources into the atmosphere as well as runoff into surface water (USDHHS, 1993). For example, as depicted in Figure 3-1 the largest use of aldrin in the United States during the 1970's was in states bordering the Great Lakes and to the south and west, the direction of most prevailing winds. Estimated trajectories of air masses, as described below (section 4.2.1.2) show that model predictions support the long range atmospheric transport of aldrin and dieldrin from these regions to the Great Lakes. In addition, urban runoff has been demonstrated to contribute a substantial amount of these chemicals to the surface waters of the Great Lakes (USDHHS, 1993).

In addition to residues from past applications, aldrin and dieldrin have been detected in soils, sediments, surface water and groundwater at hazardous waste sites in every state bordering the Great Lakes (USDHHS 1993). As discussed in Section 4.1.3, direct and indirect releases from these sites may continue to provide a source of aldrin and dieldrin to the environment.

4.2.1.2 Transport and Fate of Aldrin and Dieldrin

Atmosphere - Aldrin and dieldrin are released to the atmosphere through volatilization in both the particulate and vapor phase from previously treated soil and evaporation from contaminated surface water. Volatilization of aldrin from soil is more rapid when it is applied to the soil surface rather than incorporated into the soils. It is reported to be retarded by increasing moisture content in the soils (USDHHS, 1993). Once in the atmosphere, both chemicals may be transported great distances, and removed by wet or dry deposition (USDHHS, 1993).

Recent fluxes of dieldrin have been measured through the IADN program at 5 locations around the Great Lakes. Dieldrin associated with both wet and dry deposition and in the gas phase was measured at all locations. The highest concentrations were found in the atmosphere over Lake Michigan and Lake Erie, followed by Lake Ontario. Atmospheric back trajectories of dieldrin (Figure 4-6) show that potential atmospheric sources of dieldrin to two sites in Lake Michigan may originate far from the Great Lakes.

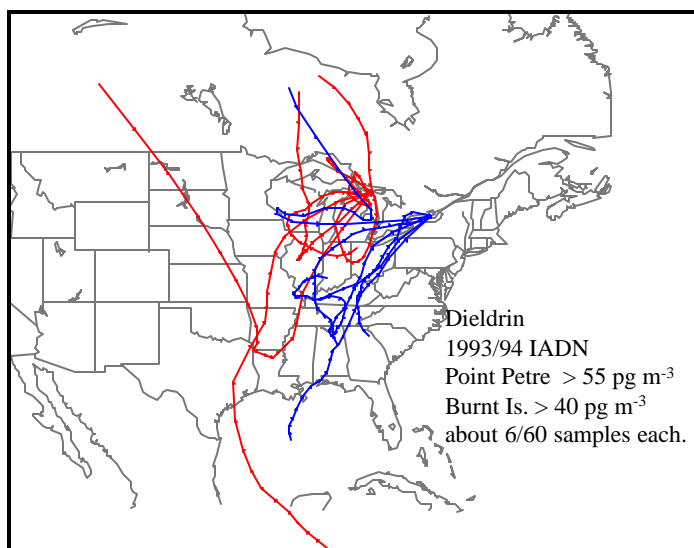


Figure 4-6. Back Trajectories of Dieldrin at Two Locations in Lake Michigan

Overall flux for the Great Lakes (except Lake Michigan, where net gas flux was not calculated) appears to be dominated by gas phase transfer out of the Lakes (IADN, 1998). This is consistent with the conclusions of Hillery, et al. (1998) for other chlorinated organics measured in the atmosphere over the Great Lakes. This trend for dieldrin was evident for data collected since 1990, although no overall decrease in either atmospheric concentrations or net flux was evident based on the average annual fluxes reported by the IADN (IADN, 1998a). However, Cortes et al. (1998) provided estimates of temporal trends based on these same measurements using partial pressures corrected for seasonal temperature. Using this approach, Cortes et al. (1998) calculated regional half-lives of dieldrin and found that there was a significant decrease of dieldrin in the atmosphere at all sites but Lake Ontario. Atmospheric half lives calculated were between 1.5 - 5.2 years, resulting in estimated dates of virtual elimination from the atmosphere ranging from approximately 2010- 2030.

Surface Water – Aldrin and dieldrin, though hydrophobic, have among the lowest K_{ow} values reported of the Level I pesticides (K_{ow} 's <4). In early studies throughout the United States, dieldrin was detected more frequently than any other Level I pesticide in all major river basins (USDHHS, 1993).

Stevens and Neilson (1989) reviewed a number of studies which measured water concentrations of aldrin and dieldrin in all the Great Lakes except Lake Michigan. L'Italien (1993, 1996a,b, 1998) reported aldrin and dieldrin concentrations in Lakes Superior, Huron, Erie and Ontario collected by Environment Canada's (EC) Ecosystem Health Department. EC sampled the lakes in multiple years. The first cruises were from 1986 through 1990 and the second set of cruises were from 1992 through 1997. Ranges of concentrations observed by decade in the various studies are presented in Table 4-4. Aldrin was detected only in Lake Superior prior to 1990. Dieldrin, however, was detected in all of the Great Lakes evaluated. Overall, it appears that concentrations have decreased in samples collected in the 1990's compared to those collected earlier. In general, however, dieldrin concentrations in the Great Lakes are higher than other Level I pesticides, except for toxaphene.

Table 4-4. Concentration Ranges in ng/L.

Pesticide	Year	Lake Superior	Lake Michigan	Lake Huron	Georgian Bay	Lake Erie	Lake Ontario
Aldrin	1992-1997	ND ^a	NA	NA	NA	ND ^b	ND ^b
Aldrin	1970-1990	0.044-0.359 ^d	NA	ND	NA	ND ^c	ND ^c
Dieldrin	1992-1997	0.07 -0.16 ^a	NA	NA	NA	0.06-0.76 ^b	0.12-0.27 ^b
Dieldrin	1970-1990	0.08-0.412 ^{d,e}	NA	0.2-0.4 ^{c,e}	0.229-0.515 ^d	0.2-1.10 ^{c,e}	0.1-0.631 ^{d,e,c}

ND Not Detected

NA Not Available

^a L'Italien, 1998

^b L'Italien, 1996a,b

^c L'Italien, 1993

^d Stevens and Neilson, 1989.

^e Hoff et al., 1996.

Sediment – Due to their hydrophobic nature, aldrin and dieldrin would be expected to accumulate in sediments of the Great Lakes. Limited sediment data exists on these chemicals. These compounds were measured in sediment cores from 5 locations in Lake Michigan (Golden, 1994). Figure 4-7 shows the concentration vs. depth profiles for these cores. The range of concentrations for both aldrin and dieldrin was relatively small and concentrations low. Aldrin was generally found at concentrations less than 2 ng/g (ppb) with little variation with depth. These data are not surprising given that aldrin is readily converted to dieldrin in the environment. Dieldrin was detected at higher concentrations showing onset of contamination in approximately the 1940s. Concentrations in cores from northern Lake Michigan generally exhibited a peak around the 1970s and then a decrease in values in recent years. Although cores from Southern Lake Michigan show similar onset as those in the north, concentrations through the 1970s to the present have remained relatively constant. This trend may be a result of greater sediment activity (e.g. resuspension, mixing) in the Southern basin rather than an indication of current inputs (Golden, 1994). This is similar to the trend seen for a number of chlorinated hydrocarbons, such as PCBs, whose input may still be significant.

Soils – Limited data regarding soil concentrations of aldrin and dieldrin from the vicinity of the Great Lakes were available. In general, because aldrin is converted to dieldrin so rapidly, aldrin concentrations tend to be much lower than dieldrin, despite the fact that aldrin was applied more frequently (USDHHS, 1993). The National Soils Monitoring Program detected dieldrin in soils at average concentrations ranging from 1 to 49 ppb in areas throughout 24 states (USDHHS, 1993).

4.2.1.3 Aldrin Trends in Fish and Birds

Aldrin is readily and rapidly converted to dieldrin in the environment, as well as in plant and animal tissues (USDHHS, 1993; Solomon et al., 1995). For example, experimental evidence indicates that 95.9 percent of radiolabeled aldrin in the fish, *Gambusia affinis* was converted to dieldrin (USDHHS, 1993). Therefore, aldrin is rarely present in environmental samples, and then only in small amounts (Solomon et al., 1995). As a result, aldrin has not been routinely monitored in fish or wildlife. No data regarding aldrin concentrations in fish or other wildlife in the Great Lakes were identified.

4.2.1.4 Dieldrin Trends in Fish and Birds

Dieldrin concentrations have exhibited a general pattern of decline in the Great Lakes since the 1970s (USEPA, 1997d; Figure 4-8a). Although the concentrations vary between lakes, a general decline with peaks in 1979 and 1984 can be observed in lake trout from Lakes Superior, Huron, and Ontario (Figure 4-8a). The largest decline in dieldrin concentration has been observed in lake trout from Lake Ontario, with a 75 percent decline since 1979. In walleye from Lake Erie, average dieldrin concentrations decreased from 0.1 mg/kg in 1977 to 0.040 mg/kg in 1982 and then increased slightly to 0.07 mg/kg in 1984. Levels declined again in 1992 to 0.03 mg/kg (DeVault et al., 1995, 1996). In Lake Michigan average dieldrin concentrations in lake trout increased from 0.27 mg/kg in 1970 to 0.58 mg/kg in 1979 followed by a decrease through 1986 (0.17 mg/kg) and 1990 (0.18 mg/kg) (DeVault et

al., 1995, 1996). A similar trend is observed in dieldrin levels in whole-body lake trout and rainbow smelt from Lake Ontario and Lake Superior, whole-body walleye from Lake Erie, and whole bloaters from Lake Michigan. In all cases, whole-body fish tissue dieldrin concentrations generally increased through 1978 followed by a steady decline (Chemical Manufacturers Association, 1997).

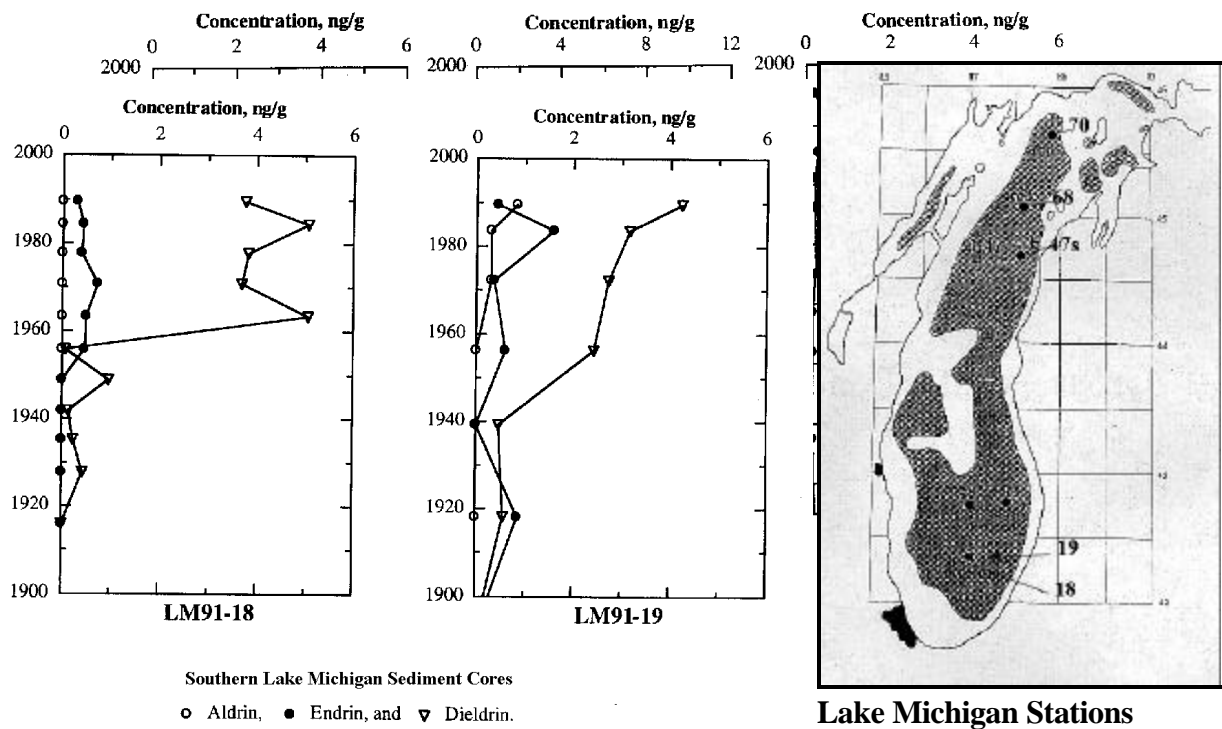


Figure 4-7. Pesticide Concentrations vs Date Profiles for Lake Michigan Sediment Cores.

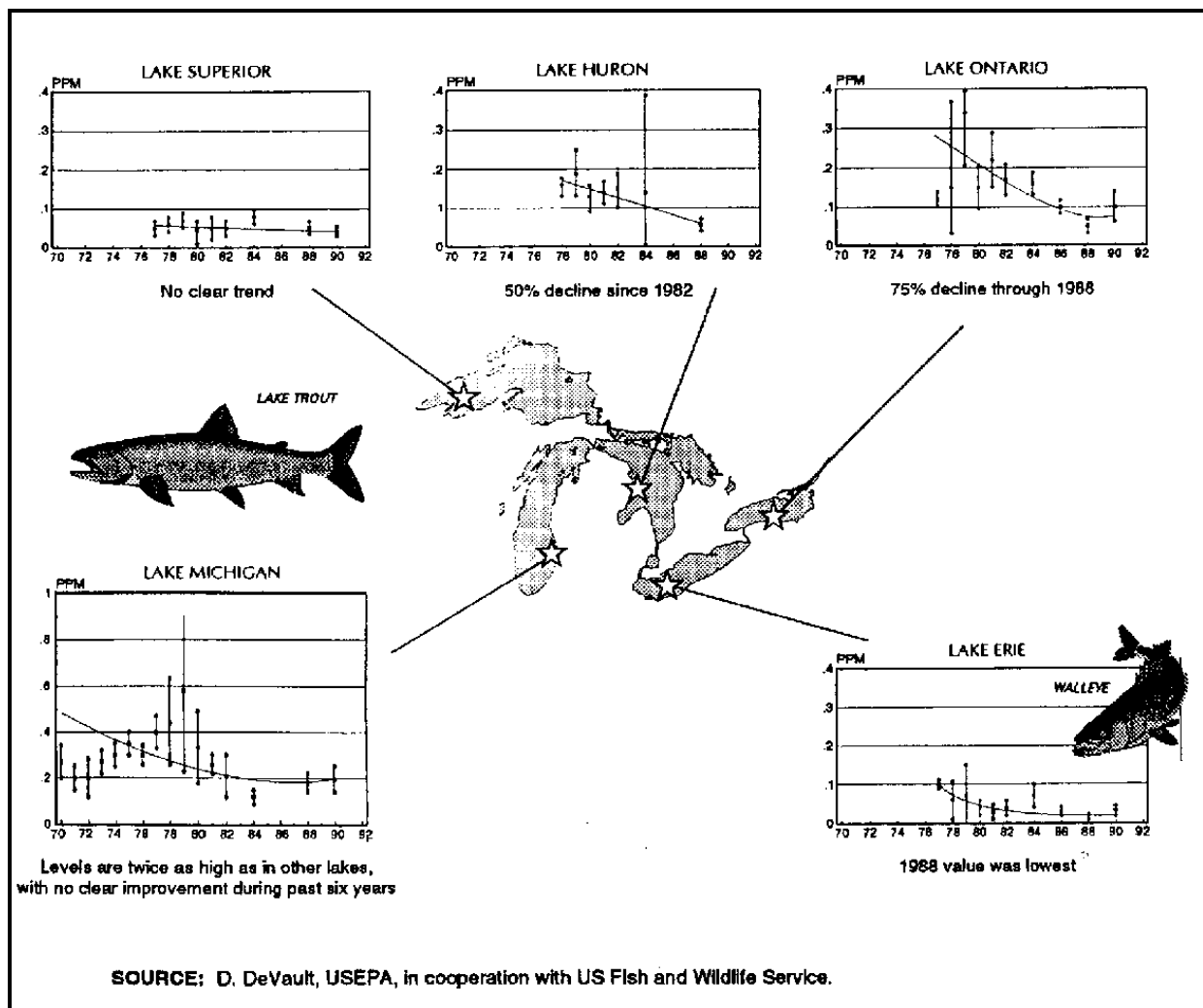


Figure 4-8a. Dieldrin Concentrations in Lake Trout from Lakes Superior, Huron, Ontario, and Michigan, and Dieldrin Concentrations in Walleye from Lake Erie.

Limited data are available regarding dieldrin concentrations in bald eagle eggs (Figure 4-8b). As bald eagles are an endangered or threatened species, systematic collection of these eggs is not possible. However, spoiled or unhatched eggs have been collected and analyzed from Lakes Superior, Erie, Huron, and Michigan. It is difficult to discern trends based on these limited data. Concentrations in eggs collected from the shoreline of Lake Erie were above 1.5 ppm in 1976 but declined to less than 0.75 ppm in 1986. However, concentrations were above 2 ppm for eggs from Lakes Huron and Michigan in 1986. Dieldrin levels in eagle eggs collected from Lake Superior in 1997 and 1998 ranged from approximately 0.5 ppm to 1 ppm, with an average concentration of approximately 0.9 ppm. The average of concentrations reported from 1986 to 1997 is 0.65 ppm.

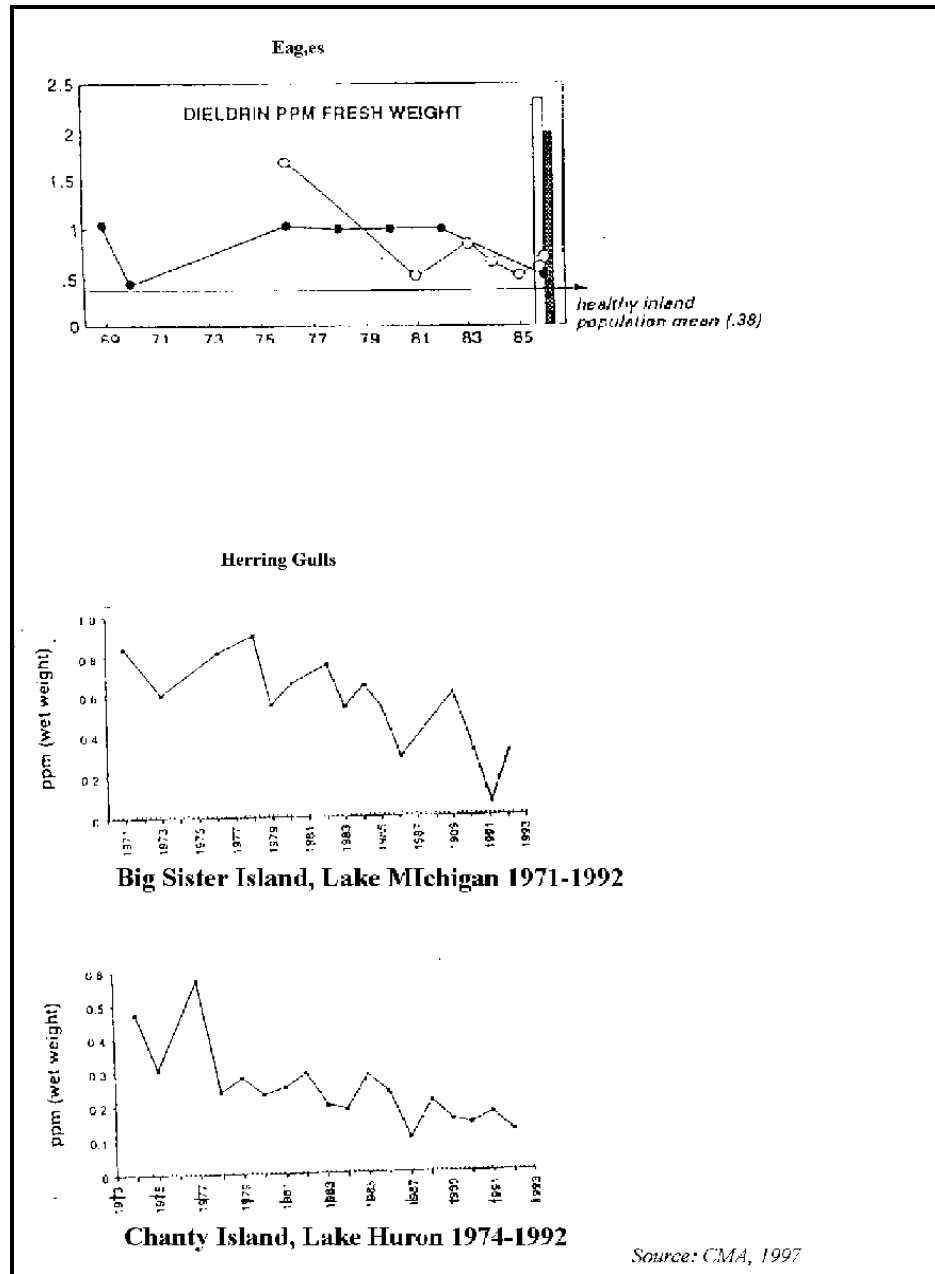


Figure 4-8b. Dieldrin Concentrations in Eagle and Herring Gull Eggs for the Great Lakes.

Herring gull eggs have also been monitored for dieldrin. Again, temporal trends are very difficult to identify (Figure 4-8b). A slow decline in dieldrin concentrations was observed in some herring gull colonies from 1971 to 1989, although in others, concentrations remain unchanged from early levels (Environment Canada, 1994). Some studies indicate a 30 percent decrease in dieldrin concentrations from 1971 to 1988 (Chemical Manufacturers Association, 1997). However, even these studies indicate a possible increase in egg concentrations in the early 1990s in all of the Great Lakes except Lakes Huron and Ontario, which remained relatively constant throughout the early 1990s.

4.2.2 Mirex

4.2.2.1 Sources of Mirex to the Great Lakes

Although actual production of mirex ceased in 1976, releases into Lake Ontario continue through leaching and runoff from dump sites adjacent to the Niagara and Oswego Rivers, both of which feed into Lake Ontario. Estimated total loading of mirex to Lake Ontario was estimated to be 2,700 kg over the last 40 years (USDHHS, 1995).

Mirex has also been detected in soils from hazardous waste sites listed in the NPL in 2 states bordering the Great Lakes (Table 4-2). Release of mirex to the atmosphere from soils throughout the United States contaminated from historical use may be a source of some mirex to the Great Lakes (USDHHS, 1995). It has been estimated that 5 percent of the total input to Lake Ontario can be attributed to atmospheric deposition (USDHHS, 1995).

4.2.2.2 Transport and Fate of Mirex

Atmosphere – Although release of mirex to the air was probably small relative to amounts released to surface water, soil and sediment, detections in air have been reported many years after production and use ceased (USDHHS, 1995). Hoff reported mean concentrations of mirex in air averaging 0.35 pg/m³ (Hoff et al., 1992a and b). However, atmospheric transport is unlikely due the hydrophobic nature and low vapor pressure of mirex; it is expected to exist mainly in the particulate phase (USDHHS, 1995). Mirex is one of the compounds measured by at least 2 IADN participants; however, no mirex results were reported.

Surface Water – Mirex is very hydrophobic and, therefore, not found to a great extent in surface water. The majority of the studies on the transport and fate of mirex have been associated with Lake Ontario and its tributaries as a result of manufacture of the compound by the Hooker Chemical Company near Niagara Falls NY. Between 1975 and 1982, mirex was detected in the aqueous phase of 6 of 22 samples in the Niagara River at levels between 0.0005 and 0.0075 ng/L (USDHHS, 1995). Mirex was found at concentrations ranging from below detection (0.06 ng/L) to 2.6 ng/L in whole water samples collected from the Niagara river between 1981 and 1983. In 1982, mean concentrations of mirex ranging from 0.00185 to 0.03 ng/L were reported in Lake Ontario, while another study reported concentrations as high as 1.5 ng/L in Lake Ontario in 1982, declining to 0.4 ng/L in 1988 (Seargent *et al.*, 1993, USDHHS, 1995). However, an intralake comparison of

concentrations in the Great Lakes conducted during 1986 did not detect mirex in any of the lakes (L'Italien, 1993, USDHHS, 1995). A more recent survey of Mirex in the Great Lakes by the USEPA Great Lakes National Program Office (GLNPO) found detectable levels of Mirex only in Lake Ontario at 0.003 ng/L, associated with the particulate fraction (Unpublished data by USEPA GLNPO, 1997). No dissolved mirex was detected.

Mudambi and Hassett (1988) reported that mirex is converted to photomirex with the loss of one chlorine atom by sunlight photolysis in Lake Ontario water. Mudambi et al. (1992) and Oliver et al. (1992) both measured mirex and photomirex in the water column of Lake Ontario and found the ratio of photomirex to mirex (P/M) was higher in the summer as compared to winter measurements, an indication of greater photolysis during periods of increased sunshine. Measurement of the P/M ratio in suspended and settling particles in the water column showed increased P/M ratios relative to surface sediments, suggesting that some of the surface sediments are being resuspended and reaching the photic zone (Oliver et al. 1989). Since P/M ratios in sediment closer to sources of mirex contamination are relatively low (e.g. indicating intact sources of mirex), the ratio of photomirex to mirex may prove useful for tracing the transport and fate of mirex in the environment. Since most mirex sources to the lake have been reduced, bottom sediments, representing historical discharges, appear to be the major source of mirex to the water column.

Sediment – Mirex is expected to accumulate in sediments in the Great Lakes based on its hydrophobic nature. It has been found at varying concentrations in the Niagara River, believed to be a major source of mirex to Lake Ontario (USDHHS, 1995). Mirex was measured in surficial sediment and sediment cores from Lake Ontario (Mudambi et al., 1992, Oliver et al., 1989). Results showed that mirex loadings from the Niagara River, a major source of mirex to Lake Ontario, had decreased by the late 1980s. Additional cores throughout the lake showed peak concentrations at depths corresponding to the mid 1960s, which agreed well with production and usage history (Figure 4-9). Based on these measurements Oliver estimated the mass of mirex contained in sediments of Lake Ontario to be on the order of 2 metric tons. This, coupled with the observation of significant sediment cycling within the lake and overall low net sedimentation, would indicate that despite probable decreases in loadings to the lake, mirex and similar chlorinated pesticides may impact the lake for many years. In contrast, concentrations of mirex in sediment cores from Lake Michigan were extremely low or not detected (Golden, 1994).

Soils – Mirex has been demonstrated to be very persistent in soils, having a half life of up to ten years (USDHHS, 1995). It has been identified in soils throughout the United States as a result of historical applications for the control of fire ants (USDHHS, 1995). However, there were no soil data identified for mirex in the vicinity of the Great Lakes.

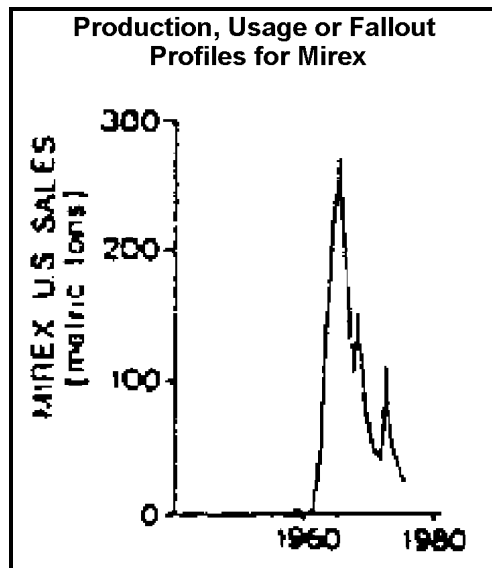
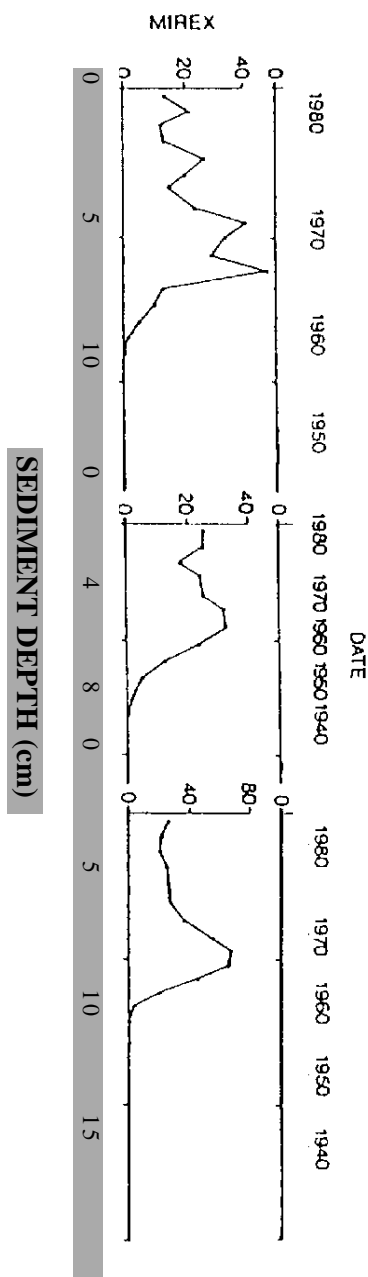
Sediment Depth Profiles for Lake Ontario

STATIONS

14
Niagra Basin

403
Mississawga
Basin

64
Rochester
Basin



Source: Oliver et al., 1989.

Figure 4-9. Comparison of Mirex Sediment Profiles from Lake Ontario with Production and Usage History.

4.2.2.3 Mirex Trends in Biota

In general, concentrations of mirex are much higher in Lake Ontario than in any of the other Great Lakes. Mirex concentrations in whole-body lake trout from Lakes Erie and Huron have been reported to be 100 to 200 times lower than those observed in Lake Ontario (Sergeant et al., 1993). Of all the coho salmon fillets collected and analyzed from the Great Lakes in 1980, only those from Lake Ontario had detectable concentrations of mirex, with an average concentration of 0.14 ppm (USDHHS, 1995). In general, levels in whole-body lake trout and spottail shiners have declined significantly since the early 1980s (Figure 4-10a).

Mirex concentrations were also monitored in herring gull eggs collected along the shores of the Great Lakes from the late 1970s to 1988 (Figures 4-10b) and showed consistent declines in concentrations since the mid-80's. However, levels in herring gull eggs from Lake Ontario have the highest mirex levels compared to levels in the other lakes by a factor of 10.

Mirex was measured in mussels at a total of 21 U.S. locations around the Great Lakes (except Lake Superior) as part of the NOAA Mussel Watch Program since 1992 (Robertson and Lauenstein, 1998). No trend information is available since most locations were only sampled once during this period. Mirex was only detected in mussels collected in Lake Ontario and in the western portion of Lake Erie and from Saginaw Bay through Lake St. Clair. Although levels found in the Lake Erie area were lower than those found in Lake Ontario, they may indicate releases of mirex have occurred in the vicinity of these sites. This is supported by sales records reported by Environment Canada's Report on Mirex (Environment Canada 1977). Data in this report indicated that the bulk of the mirex sold in the Great Lakes basin was to a company in Adrian, MI., which is located just southwest of Detroit and in close proximity to the sites described above.

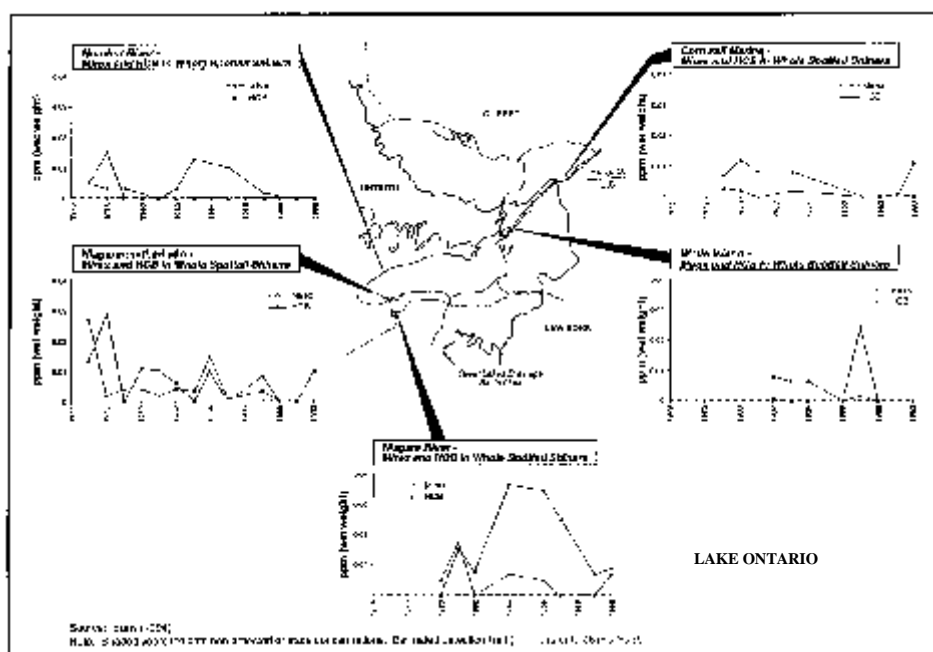


Figure 4-10a. Changes in Mirex Levels in Spottail Shiners from Lake Ontario, 1977-1990.

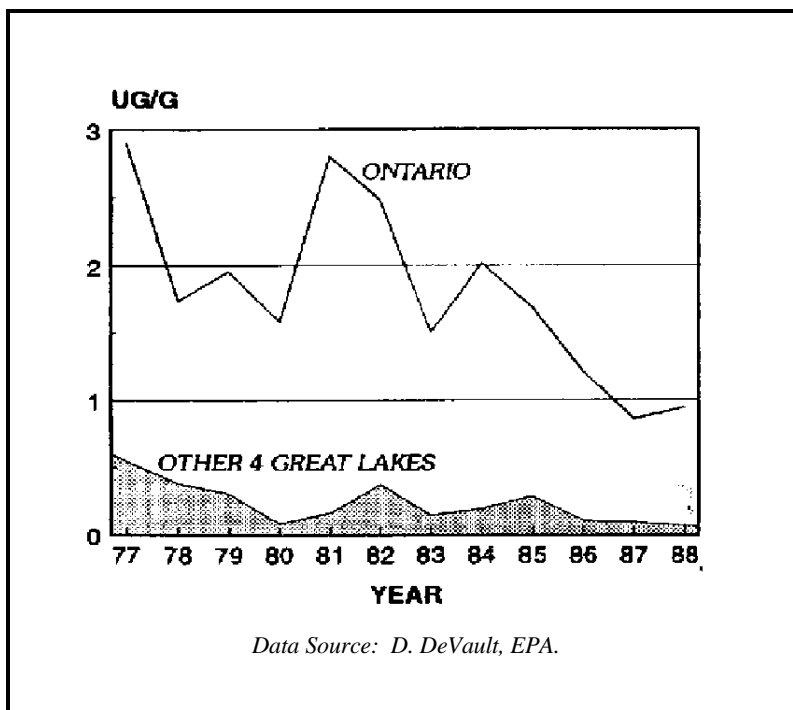


Figure 4-10b. Mirex in Herring Gull Eggs for the Great Lakes.

4.2.3 Chlordane

4.2.3.1 Sources of Chlordane to the Environment

Prior to 1978, chlordane was used as a pesticide on agricultural crops, lawns and gardens and as a fumigating agent. From 1983 to 1988 its only approved use was as a termiticide applied underground around the foundation of homes (USDHHS, 1994a). Since 1988 all uses have been prohibited in the United States, although chlordane is still manufactured for export to other countries.

Current sources of chlordane to the Great Lakes are generally from historical use or production of the compound. Documented releases of chlordane to the environment from US production and handling facilities, according to the 1990 TRI, indicated that a total of 4,423 lbs were released to the air. On the basis of historic production figures, an estimated 70,000 tons of chlordane were produced since 1946, of which 25-50 percent is estimated to still exist unaltered in the environment (Dearth and Hites, 1991b). Although no estimates of the percentage of application relative to the Great Lakes Region are available, the primary applications were generally south and west of the region, coinciding with termite infestation.

In addition to sources associated with direct releases and historical applications, chlordane has been identified in at least 176 of the 1,350 hazardous waste sites that have been proposed for inclusion on the EPA's NPL, many of which are located in States bordering the Great Lakes (Figure 4-6; USDHHS, 1994a). Although chlordane exists primarily in the vapor phase and is susceptible to rapid photo degradation in this state, the small amount bound to particles appears to be significant in terms of

long range transport of chlordane (Atlas and Giam, 1988). Uses of chlordane in other parts of the world still act as sources to the Great Lakes through atmospheric transport.

4.2.3.2 Transport and Fate of Chlordane in the Environment

Atmosphere – If released to the atmosphere, chlordane exists predominately in the vapor phase. Degradation in the vapor phase, however, is relatively rapid with half-lives of 1.3 - 6.2 hr for technical chlordane (USDHHS, 1994a). The amount of chlordane bound to particulates in the atmosphere relative to the amount in the vapor phase, however, is temperature dependent and has been reported to range from less than 1 percent in temperate regions to approximately 45 percent in colder, arctic regions (Patton, et al. 1991, USDHHS, 1994a). The small amount adsorbed to particles under temperate conditions appears to play an important role in atmospheric deposition. Air samples taken in Belize, Central America in 1995 and 1996 showed many persistent chlorinated pesticide concentrations significantly elevated in the Central American samples (10-50 times) relative to the Great Lakes levels measured by the current IADN program (IADN, 1998a). However, concentrations of chlordane were generally at or only slightly above Great Lakes levels (Bidelman, 1998).

Chlordane concentrations in home air are often 10-1000 times higher than in ambient air (USDHHS, 1994a) and outgassing from buildings treated for termites may be a significant source of chlordane release to the environment. Even though recent use of chlordane for this application has been stopped, studies have detected chlordane in indoor air of homes treated for termites up to 15 years after application. Interestingly, the pattern of enantiomeric ratios (ER) (as discussed below under “Soil”) in air from these homes has been observed to be similar to the ratios in the original products (e.g. 1:1), which is different than ratios found in soils and air close to agricultural sources of chlordane. These residue patterns can be followed during volatilization and atmospheric transport to differentiate chlordane originating from various uses such as historical or recent agricultural application or termite control.

Cortes et al. (1998) measured concentrations of a number of chlorinated pesticides including the three chlordane related compounds (*a*- and *g*-chlordane and *trans* nonachlor) in the atmosphere seasonally from January 1992 - December 1994. Samples were collected at the 5 IADN sites (IADN, 1998a). The overall trend showed significant decrease of these compounds at 2 of the 5 locations (those in lakes Erie and Ontario) with half-lives ranging from 3.2-9.2 yrs. Where decreases were significant, an estimate of the time it would take for virtual elimination of these compounds was made. Dates of virtual elimination (based on a detection limit of roughly 0.1 pg/m³) from the atmosphere ranged from 2010-2050, depending on the compound and the measured concentrations present. Significant decreases were not observed at the locations in Lakes Superior, Michigan and Huron.

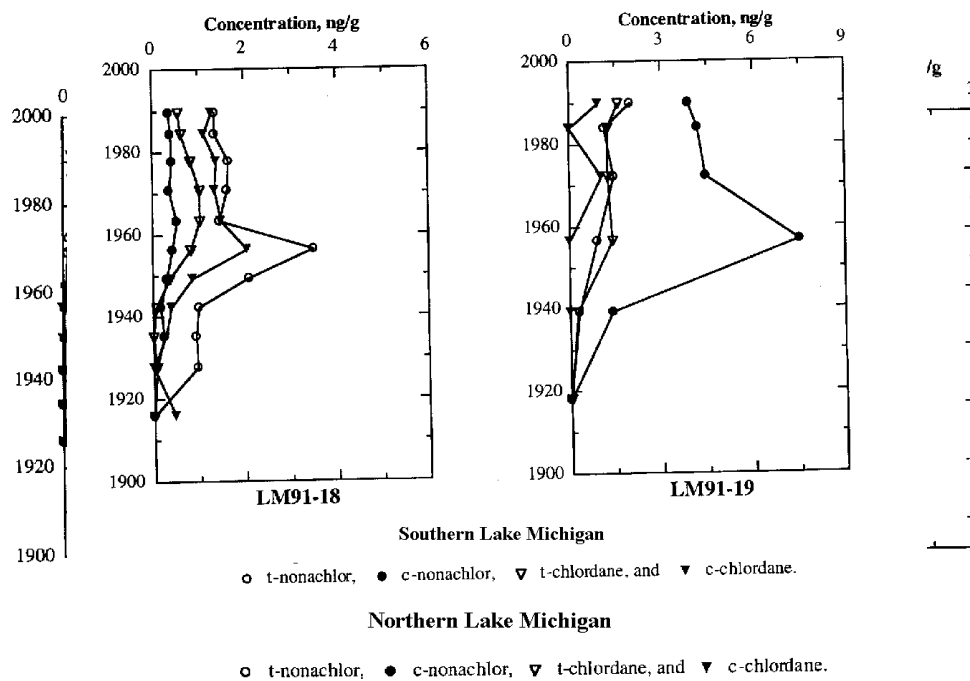
Surface Water – Chlordane has been detected prior to 1990 in waters of the Great Lakes at concentrations ranging from not detected to 0.3 ng/L, measured as *cis* and *trans*-chlordane (Stevens and Neilson, 1989). In general, levels of the *cis* isomer are approximately two to three times higher than those of *trans*-chlordane (Stevens and Neilson 1989). Based on the low solubility and high K_{ow} of chlordane any chlordane present in the water column is likely bound to particles and is expected to

partition to sediments. Recent measurements of chlordane were made in Lake Superior in 1996 and 1997 (L'Italien, 1998). Only *cis*-chlordane was detected at concentrations ranging from 0.006 to 0.011 ng/L in a limited number of the total stations sampled. Additional sampling of all of the Great Lakes was performed by USEPA Great Lakes National Program Office (GLNPO). Total chlordane was detected in both the dissolved and particulate fractions collected. Total concentrations (dissolved plus particulate) ranged from approximately 0.008 ng/L in Lake Superior to 0.026 ng/L in Lakes Michigan and Erie.

Sediment – Sediment concentrations measured from Great Lakes harbors ranged from 1.5 to 310 ppb (Puri et al., 1990). Surficial concentrations of four chlordane related compounds measured by Golden (1994) in Lake Michigan's southern and northern basin ranged from approximately 0.5 to 4 ppb. Concentrations of these components were also measured in sediment cores from five locations around Lake Michigan. Figure 4-11 shows the concentration vs. depth profiles from these cores. In most locations, *cis*-nonachlor was the dominant isomer. These profiles identify the 1940s as the onset of contamination with maximum concentrations occurring between 1960 and 1980. Concentrations associated with more recent sediments are lower, reflecting the decreased domestic use as a result of increasing regulation.

Soil – If released to soil, chlordane persists for long periods. Under field conditions, the observed mean degradation rate ranges from 4.05-28.33%/yr with a mean half-life of 3.3 years. Chlordane has been found in soils upwards of 20 years after application, and chlordane, like many of the persistent chlorinated hydrocarbons, persists much longer in heavy soils with high organic content vs. loamy sandy soil. (USDHHS, 1994). Chlordane concentrations have been reported in rural and urban soils ranging from < 1 ppb to 141 ppm, with concentrations in soils in the Great Lakes States somewhat lower (0.05-10 ppm). However, these measurements were made in the 1960s and 1970s and generally mirrored use patterns. Very few recent soil monitoring data are available. However, what is available shows that chlordane is still present (USDHHS, 1994).

Only limited degradation information is available. It has been suggested that chlordane is very slowly biotransformed in the environment, which is consistent with the long persistence periods observed under field conditions. Recent investigations (Uhlrich and Hites, 1998) have shown that metabolization by soil microorganisms produce a different pattern of residues that can be followed during volatilization and atmospheric transport. Each isomer of chlordane consists of two right- and left-hand, mirror-image molecules called enantiomers (two for *cis*-chlordane and two for *trans*-chlordane). In technical chlordane, these enantiomers are in exactly a 1:1 ratio (racemic mixture), and this ratio is not changed by purely chemical or physical process (eg. hydrolysis, photolysis, volatilization or deposition). Only metabolism, an enzymatic mechanism, has the ability to change the enantiomer ratio (ER) from the 1.0 value of the original product.



Source: Golden, 1994.

Figure 4-11. Chlordane Concentrations vs Date Profiles for Lake Michigan Sediment Cores.

Comparison of enantiomeric ratios (ER), therefore, can be used to differentiate chlordane originating from various uses such as historical or recent agricultural application or termite control. In technical chlordane, the ER ratio is 1:1 (e.g. racemic). The chlordane residues measured in midwestern soils (the "Cornbelt"), often have ER values that are significantly different than 1.00 (Aigner et al., 1998). In addition, the chlordane residues measured in air over these soils also show this pattern. By contrast, the chlordane emitted from termiticide usage is racemic (e.g. little metabolism has occurred, most likely due to the high levels of the product present which reduces biological activity) (Bidelman et al., 1998). The chlordane found in ambient air over the Great Lakes has ER values that are intermediate between agricultural soils and home air, and thus appears to contain a mixture of chlordane emitted from historical agricultural use and racemic sources (e.g. termiticide usage, spills/hot spots and/or new applications outside the U.S.). Measurement of the ER can be used as a tracer of agricultural (crop pesticide) vs. urban application (termiticide). Though the magnitude of this biodegradation is not documented, the formation of a "traceable" signature of soil-derived chlordane is significant.

4.2.3.3 Chlordane Trends in Fish and Birds

Nearly all long-term monitoring studies have indicated a decline in the concentrations of chlordane in fish from the mid-1970s through the early 1990s. Oxychlordane, a metabolite of chlordane, has been monitored in fish in Lakes Superior, Erie, and Michigan since 1977, since 1978 in Lake Huron, and since 1986 in Lake Ontario (Figure 4-12a). A significant decrease in mean oxychlordane concentrations was observed in whole-body fish tissues from each lake during the time period evaluated. In Lake Superior, oxychlordane concentrations in whole-body lake trout increased from 0.1 in 1977 to 0.4 ppm in 1978, then decreased to 0.02 ppm in 1980 (DeVault et al., 1986). Oxychlordane concentrations in whole-body lake trout from Lake Michigan, decreased from a mean concentration of 0.2 ppm from 1977 through 1979 to 0.05 ppm in 1981 (DeVault et al., 1986).

Like oxychlordane concentrations, chlordane concentrations in whole-body fish tissue have also shown declines. Chlordane concentrations in whole-body lake trout from Lake Superior declined from a high of 0.1 ppm in 1976 to essentially not detectable in 1984 (Chemical Manufacturers Association, 1997). In Lake Huron, chlordane concentrations in whole-body lake trout also showed a steady decline from 0.2 ppm in 1979 to approximately 0.01 ppm in 1992. Chlordane concentrations in whole-body lake trout from Lake Ontario have remained fairly constant (approximately 0.1 ppm) from 1979 to 1988 with a peak of 0.13 ppm during 1983 (Borgmann and Whittle, 1991). In spottail shiners, chlordane was not detectable by the late 1980s (Chemical Manufacturers Association, 1997).

Studies of herring gull eggs have reported a slightly different trend. Chlordane levels in herring gull eggs increased or remained constant from the mid-1970s to 1980 before dropping dramatically. Oxychlordane levels in herring gulls eggs from several gull colonies were above 0.3 ppm in Lakes Ontario, Michigan, Erie, and Huron in the mid-1970s and have declined to or below 0.1 ppm in all of the lakes except Lake Michigan (Figure 4-12b). Concentrations in herring gull eggs from Lake Michigan have declined from levels close to 1 ppm in 1982 to about 0.25 ppm in 1989 through 1992 (Chemical Manufacturers Association, 1997).

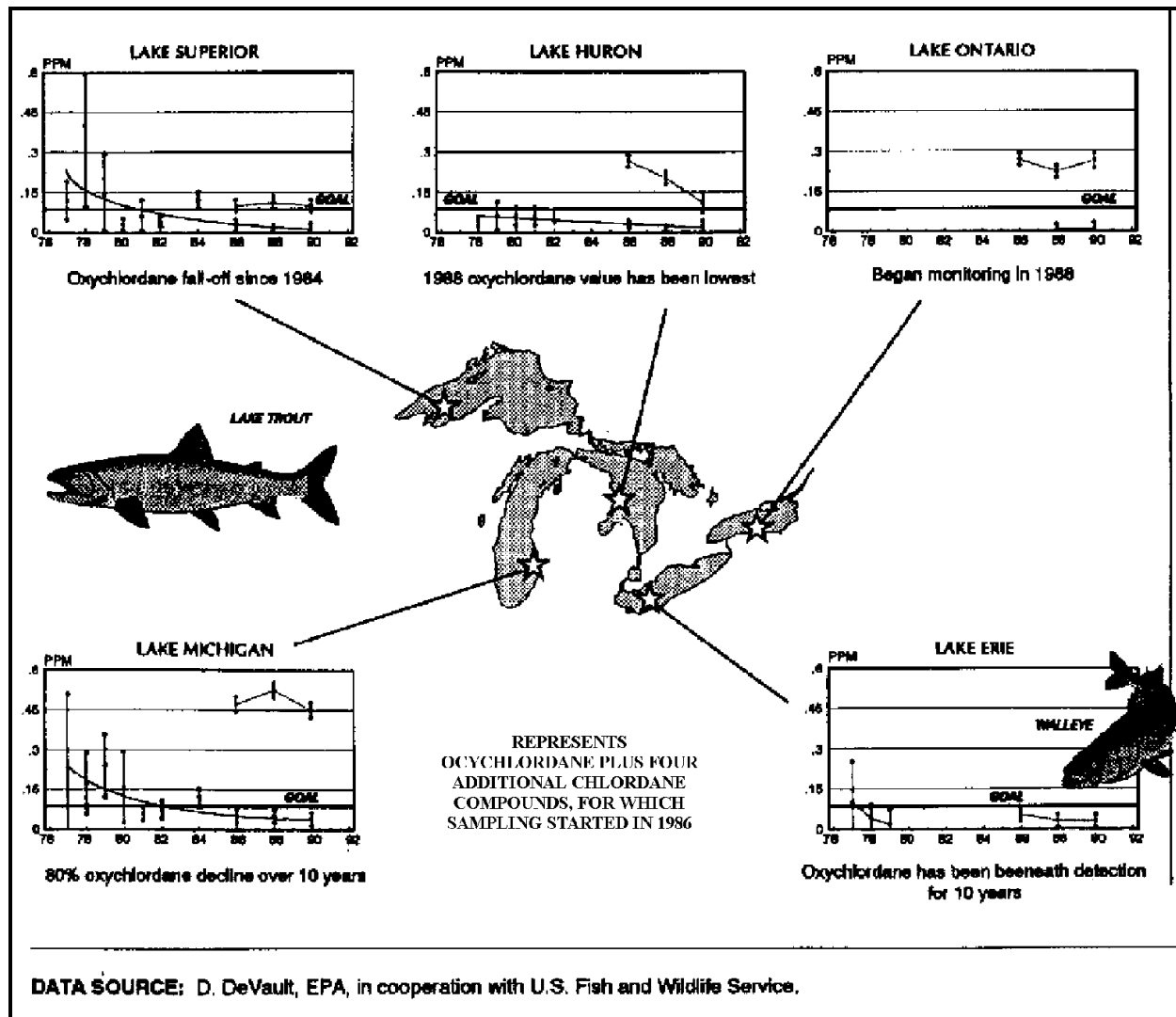


Figure 4-12a. Oxychlordanes Concentrations in Lake Trout from Lakes Superior, Huron, Ontario, and Michigan, and Oxychlordanes Concentrations in Walleye from Lake Erie.

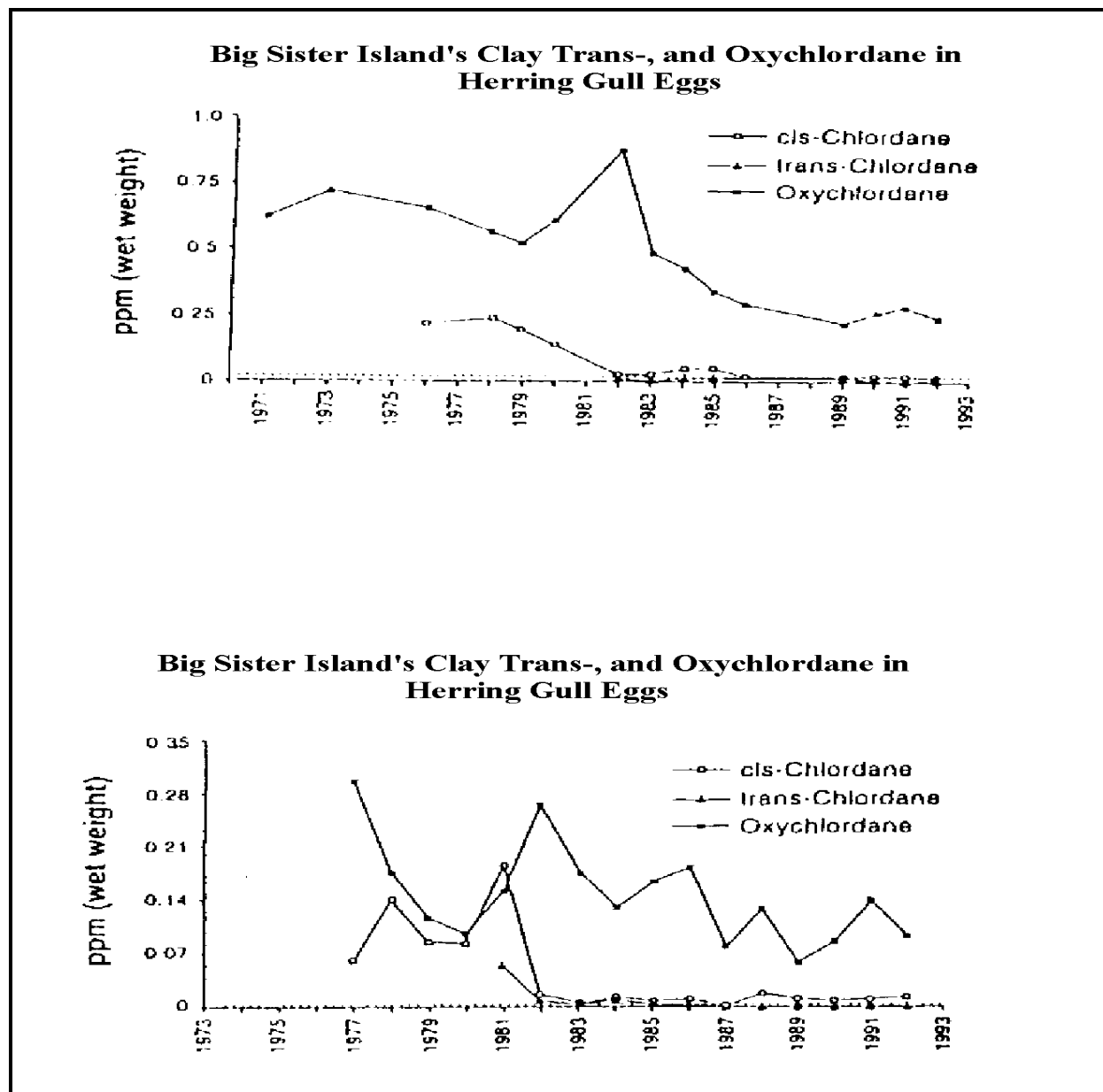


Figure 4-12b. Chlordane Concentrations in Herring Gull Eggs.

4.2.4 DDT

4.2.4.1 Sources of DDT to the Environment

Historically, DDT was used extensively throughout the United States. It has been estimated that more than 2 billion kg of DDT was used for insect control between 1940 and 1973 (USDHHS, 1993). Domestic use of DDT was canceled in the 1970's, however, as previously discussed, global use has continued. As a result, production of DDT for export continued in the United States long after domestic applications ceased. There are currently no known producers of DDT in the United States; however, as recently as 1985 there were two production sites totaling 303,000 kg of DDT for export (USDHHS, 1993). Global use trends also generally show a decline (Loganathan and Kannan, 1994). However, measurable amounts of DDT and its metabolites are still found in the air, water, sediment and soil in and around the Great Lakes. During the 1980s, it appeared that the atmosphere was actually a sink for pesticides volatilizing DDT from the Great Lakes (Hillery et al., 1998). However, recent measurements show that decreasing water column concentrations appear to have reversed that trend and the net flow of DDTs are, for the most part, into the Lakes. This pattern of flow into and out of the Lakes is partially seasonal and with continued global use, the potential is for the atmosphere to remain a source of DDTs to the Great Lakes.

Hazardous waste sites, both terrestrial and aquatic, have the potential to act as sources of hydrophobic organic contaminants such as DDT to the environment through run-off and volatilization. As discussed in Section 4.1.5, there are 3 NPL sites in Michigan that reported DDT contamination in sediment, soils or groundwater. Direct and indirect releases from these and similar sites may continue to provide a source of DDT to the environment.

4.2.4.2 Transport and Fate of DDT in the Environment

Atmosphere – Volatilization of DDT from soil surfaces and water is known to occur (USDHHS, 1993). Once in the atmosphere, DDT will eventually photo oxidize to carbon dioxide and hydroxyl radicals, with an estimated half-life of approximately 2 days for the latter. However, the presence of DDT in samples far from known sources indicates that DDT photo degradation is slower than estimated (USDHHS, 1993). Both wet and dry deposition are significant mechanisms of removal from the air column.

Measured atmospheric concentrations of DDT and its metabolites have, as in other compartments, shown a steady decrease since cancellation of domestic use and restrictions in other countries. Cortes et al. (1998) measured concentrations of a number of chlorinated pesticides including the DDT isomers and its metabolites in the atmosphere seasonally from January 1992 - December 1994. Samples were collected at the 5 IADN sites (IADN, 1998a). Cortes et al. (1988) showed that there is significant decrease of the p,p'-DDT compounds at most sites with half lives ranging from 2.5-2.7 years. p,p'-DDE, the primary metabolite of p,p'-DDT, is not declining as rapidly at most sites with half lives ranging from 5.1-9.2 yrs. Based on these observations and calculations, estimated dates of virtual elimination from the atmosphere were reported. In general, DDT and DDD will be the first to disappear at all sites, in about 2010. Virtual elimination dates for p,p'-DDE occur later (from 2010 to 2070, depending on location) at all sites due to its higher atmospheric concentrations and longer half-life.

Although overall atmospheric concentrations of DDT are decreasing (Cortes et al., 1998), the relative importance of atmospheric flux as both a source and a sink of DDTs to the Great Lakes is becoming more significant. Atmospheric loadings measured pre-1990, showed significant net loading out of all 5 of the Great Lakes as compared to the more recent findings (Hillery et al., 1997). This may be a reflection of the higher DDT water concentrations during this period due to historical domestic uses. More recent data show net deposition of total-DDT was substantially into Lakes Superior, and Erie and that wet and dry deposition, at least, accounted for a significant input to Lake Michigan (Table 4-5). Total-DDT transport was slightly out of Lake Huron while the net flow between Lake Ontario and the overlying atmosphere was not significantly different from equilibrium. The subsequent change in net direction of flow of DDT reflects the decline in water concentrations with decreased domestic use.

Table 4-5. Air/Water Exchange Rates of DDT in the Great Lakes^a

(Negative numbers indicate net loss from lake to atmosphere. Bold entries are significantly different from zero.)

Year	Superior (kg/yr)	Michigan	Huron	Erie	Ontario
Pre-1990	-650	-460	-470	-200	-150
1991-1992	47 ±45	99 ±140	37 ^b	81 ±50	-140 ±150
1993-1994	70 ±35	76 ±90	-36 ±37	110 ±63	-11 ±30

^a Data from Hillery, et al., 1997;

^b Wet deposition only.

Though overall loadings of DDTs from the atmosphere are declining, some elevated concentrations of DDT have been observed around the Great Lakes. Significantly elevated levels of total-DDTs have been measured in air near South Haven, Michigan relative to other locations in the Great Lakes Basin (proposal from MDEQ, 1998). Recent levels at South Haven are also substantially greater than ambient levels that were monitored during the early 1970s at the time of peak DDT use. The range of 24-hr maximum values measured in northern Michigan by the MDEQ from 1992-1994 ranged from 0.030 to 0.076 ng/m³ compared to 0.986 ng/m³ measured at a site near South Haven. Though the reason for these elevated levels has not been determined, it is hypothesized that either the DDTs are volatilizing from contaminated soils during certain tillage practices, are being transported from other locations or may be a result of legal application of the pesticide dicofol, which contains trace levels of DDT as a contaminant. Additional investigations of the air, soil and vegetation in this area are currently under way.

Surface Water – DDT reaches surface waters primarily by runoff, atmospheric transport, drift, or by direct application (e.g., to control mosquito-borne malaria). The reported half-life for DDT in the water environment ranges from a few days for fast-moving environments (where the compound is at or near the surface of the water) to more than 150 years (Spectrum Laboratories, 1998). The main degradation and loss pathways in the aquatic environment are volatilization, photo degradation, adsorption to water-borne particulates (including sedimentation) and uptake by aquatic organisms, which store DDT and DDT metabolites in their tissues.

Information from data collected between 1980 and 1983 indicated that DDT was widely detected in ambient surface water samples in the United States at a median level of 1 ng/L (part per trillion) (USDHHS, 1993). Concentrations in the Great Lakes are generally lower. A summary of average water concentrations for five of the Great Lakes separated by pre- and post-1990 measurements (Table 4-6), indicates that neither DDT or DDE were detected in the water column of any of the lakes above 0.06 ng/L (USEPA, 1997d). In general, it appears that levels of DDTs in the water column of the Great Lakes is variable. Concentrations appear to be decreasing in Lakes Superior, Huron and Erie, however, limited available data make it difficult to interpret trends.

Table 4-6. DDT Concentration Ranges in ng/L.

Pesticide	Year	Lake Superior	Lake Michigan	Lake Huron	Lake Erie	Lake Ontario
DDT	1997 ^f	0.006	0.039	0.014	0.063	0.043
DDT	1990-1997	< 0.06 ^{a,e}	0.005 ^e	0.002 ^e	0.002- 0.3 ^{b,d}	0.004 ^e
DDT	1970-1990	0.007-0.195 ^{c,d}	NA	0.002-0.15 ^{c,d}	0.007-0.22 ^{c,d}	0.02-0.05 ^{c,d}

ND Not Detected

NA Not Available

a L'Italien, 1998

b L'Italien, 1996

c L'Italien, 1993

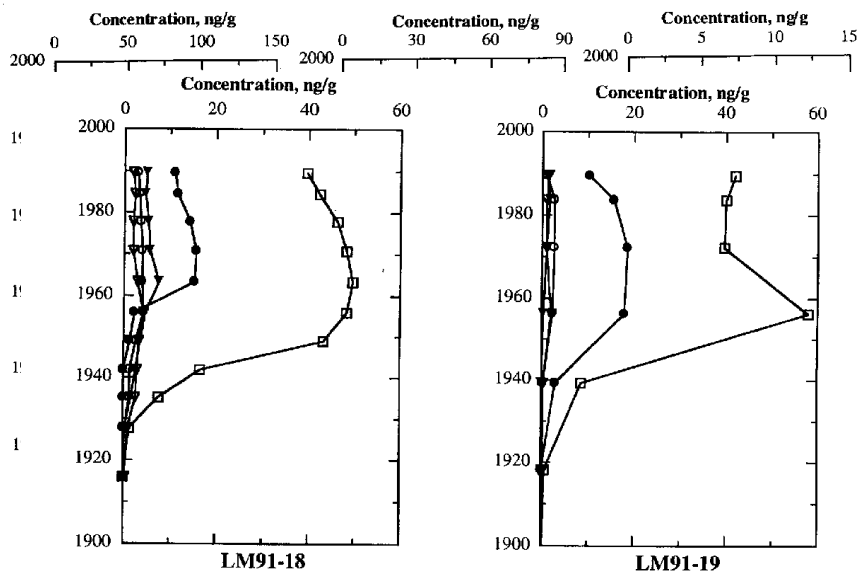
d Stevens and Neilson, 1989.

e Hoff et al., 1996

f USEPA, Great Lakes National Program Office; Unpublished Data

Sediment – Golden et al. (1993) measured DDT and its metabolites in sediment cores from Lake Superior, Lake Michigan and Lake Ontario (Figure 4-13). Total DDTs in surficial sediments from Lakes Michigan and Ontario were 50 ppb and approximately 3 ppb in Lake Superior. The onset of DDT occurrence in these sediment cores is approximately 1940 to 1950, with the most rapid increase in concentrations occurring from 1960 to 1970 in all the cores. Consistent with past sediment cores taken in the region as well as terrestrial cores taken from peat bogs in the mid-latitudes of North America, these data indicate that the majority of the input was most likely atmospheric. Rapid decreases observed in concentrations correspond with the cancellation of DDT use in 1972. However, both sediment cores from the north basin of Lake Michigan show unexpectedly high historical concentrations of DDT when compared to southern basin cores, most likely a result of inputs from the Fox River and Green Bay area.

Figure 4-13.
Metab
Concen
Date
Lake
Sedime



Southern Lake Michigan

○ op' DDT, ● pp' DDT, ▼ op' DDD, ▼ pp' DDD, and □ pp' DDE.
Source: Golden 1994.

DDT
olite
trations vs
Profiles for
Michigan
nt Cores.

The rate of decrease in DDT concentrations in sediments of southern Lake Michigan has slowed considerably over the last decade and the continued elevated levels are probably due to continued inputs to the basin and long term movement of contaminated sediments to the main depositional basin. Eadie et al. (1998) documented a major resuspension event in the spring months in the southern basin of Lake Michigan. This coastal turbidity plume persisted for over a month, progressing northward along the eastern shore. This event illustrates the process by which the large inventory of constituents stored in temporary sediment deposits can be re-supplied to the water column and redeposited into more permanent depositional environments, such as exists in the northern basin. This large resuspension and mixing event, if an annual occurrence, may also account for the slower decline in surficial sediment concentrations observed in the southern basin.

Soil – DDT is very persistent in soil, with a half life estimated between 2 and 15 years. Routes of loss and degradation include runoff, volatilization, photolysis and biodegradation (aerobic and anaerobic). These processes generally occur very slowly. DDE and DDD are the initial breakdown products of DDT in the soil environment. Both sister compounds are also highly persistent, and have chemical and physical properties similar to DDT. Due to its extremely low solubility in water, DDT will be retained to a greater degree by soils and soil fractions with higher proportions of organic matter. Highly organic soils treated with DDT will tend to retain the pesticide and its byproducts in the surface layers.

As with many other chlorinated organic chemicals, DDT sorbs tightly to organic matter. Because of the compound's persistence, wind and water erosion have made the compound virtually ubiquitous in the environment. Over very long periods DDT can eventually leach into groundwater, especially in soils low in organic matter. Residues in surface soils are much more likely to be broken down or otherwise dissipated than in subsurface deposits. Studies in Arizona have shown that volatilization losses may be relatively fast (50 percent in 5 months) in soils with very low organic matter content (desert soils) and high irradiance of sunlight. In other soils (e.g., Hood River and Medford, OR) this rate may be as low as 17-18 percent over 5 years. In summary, volatilization loss depends on the amount of DDT applied, proportion of soil organic matter, proximity to soil-air interface, and the amount of sunlight.

There are no soil data available for the Great Lakes region. Available data from throughout the United States indicate that concentrations in the 1970s averaged from 0.02 ppm to 0.18 ppm (USDHHS, 1993).

4.2.4.3 DDT Trends in Fish, Birds and Bivalves

DDT is very lipophilic and, therefore, readily bioaccumulates in fish and other aquatic organisms. In aquatic systems, DDT and its metabolites are bioconcentrated in aquatic organisms, and biomagnify in the food chain (USDHHS, 1993). The evaluation of DDT trends in wildlife is complicated by the fact that some studies report total DDT (DDT and the sum of metabolites) whereas other studies may report DDT, DDE, and DDD separately. Generally, trends observed in metabolites will reflect trends of the parent compound. However, absolute concentrations are not always comparable.

Fish – In general, total DDT concentrations in whole-body fish tissue have declined in all lakes over the last two decades (Figure 4-14a). The largest decline has been observed in Lake Michigan where lake trout levels have dropped 85 percent since 1973. Total DDT concentrations in Lake Michigan lake trout dropped from 19.19 ppm in 1970 to 1.39 ppm in 1990 and 1.16 ppm in 1992 (DeVault, et al., 1995, 1996). Similar trends were seen in Lakes Superior, Huron, and Ontario (DeVault, et al., 1996). Similar trends have also been observed in other fish species. The Ontario Ministry of the Environment and Energy monitors young of the year spottail shiners. These fish live in local near-shore areas and do not travel extensively during their year of life. Total DDT concentrations have declined significantly from the 1970's through 1990 (DeVault, et al., 1995). DDT levels have also been routinely monitored in rainbow smelt by Fisheries and Oceans Canada since 1977. Top predator fish (lake trout, coho salmon, and walleye) forage on these lower trophic level fish. DDT levels in these fish have significantly decreased in Lakes Superior, Huron, Erie, and Ontario. Levels in Lake Ontario are consistently the highest (DeVault et al., 1995). In coho salmon fillets, DDT trends in Lake Michigan seem to be following a pattern consistent with PCBs. That is, statistically significant declines were observed from 1980 through 1984 followed by no statistically significant change (DeVault et al., 1995). The correlation between PCB and DDT trends suggests a change in the composition of the food web (DeVault et al., 1995).

The most recent available data indicates that DDT levels in fish appear to have leveled off. For example, there has been little change in DDT concentrations in lake trout since the late 1980s. In addition, while a statistical trend analysis of data for walleye from Lake Erie indicate a significant loss rate from 1977 through 1982, there has been no significant change in the mean DDT levels since that time (DeVault et al., 1996). Only in Lake Huron do the data suggest a continuing decline in DDT level in lake trout (DeVault et al., 1995).

Herring Gulls – In addition to fish, herring gulls, a fish-eating bird, have been monitored by the Canadian Wildlife Service since the early 1970s for exposure to DDT and its metabolites (Figure 4-14b). Concentrations of DDE, a metabolite of DDT, in herring gull eggs has declined significantly between 1974 and 1993 (DeVault et al., 1995). As observed in the fish tissue levels, the highest rate of decrease was observed between 1974 and 1980s. Since then the rate of decrease has been much slower (DeVault et al., 1995; Environment Canada, 1994).

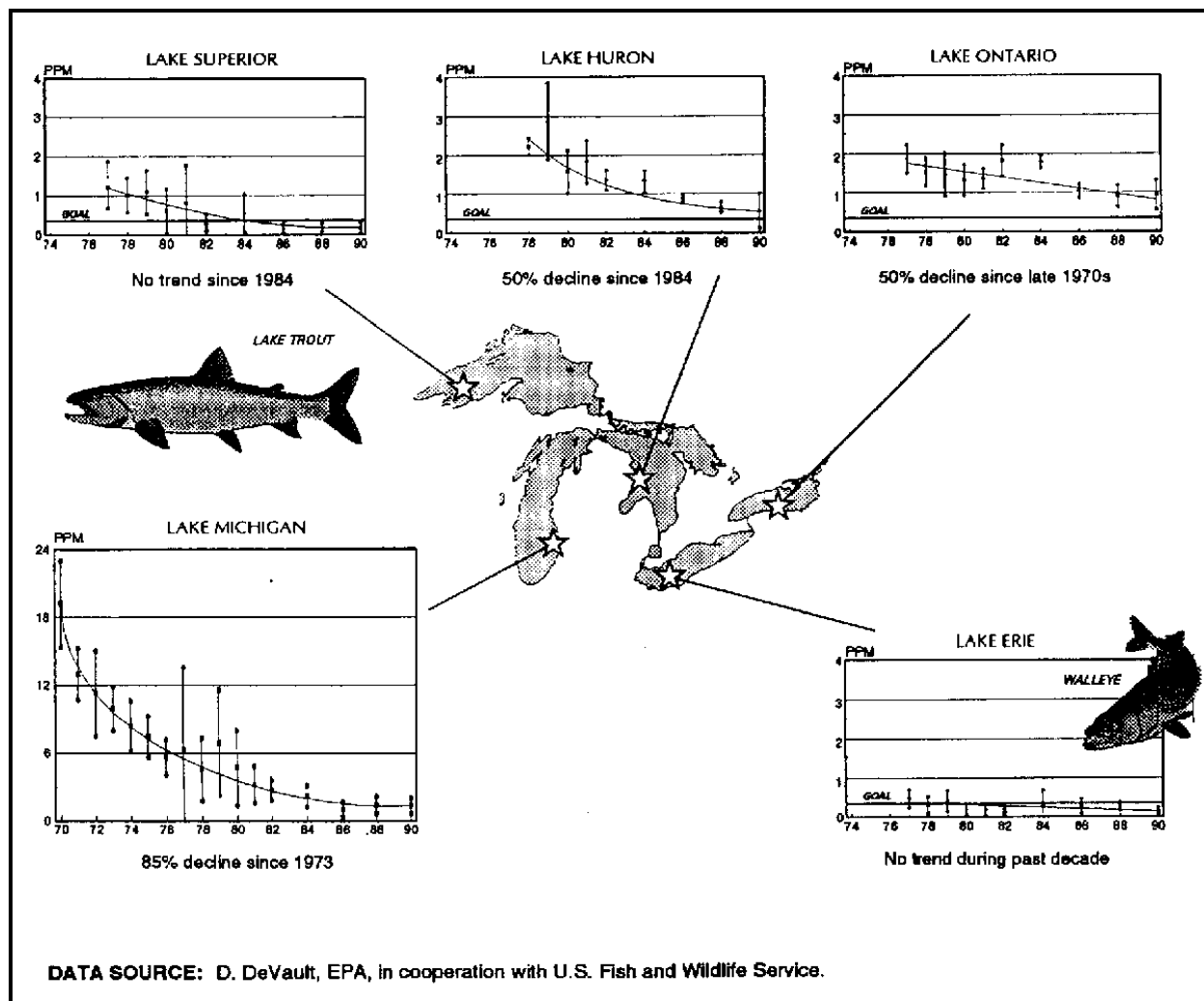


Figure 4-14a. Concentrations of Total DDT in Lake Trout from Lakes Superior, Huron, Ontario, and Michigan and Concentration of Total DDT from Walleye in Lake Erie.

Eagle Eggs – The DDT metabolite, DDE, has also been measured in bald eagle eggs from Lakes Superior, Erie, Huron, and Michigan (Figure 4-14c). As mentioned previously, the endangered or threatened status of bald eagles prohibits systematic sampling or monitoring; however, spoiled or unhatched eggs are occasionally available for sampling. DDE concentrations from eggs collected from the shoreline of Lake Superior have declined from 40 ppm in 1969 to approximately 10 ppm in 1986. Levels in eggs collected from the shoreline of Lake Erie decreased from above 20 ppm to 3.9 ppm in 1984 and then increased to approximately 10 ppm in 1986. DDE concentrations in eagle eggs collected in 1986 from Lakes Huron and Michigan were both above 30 ppm in both lakes.

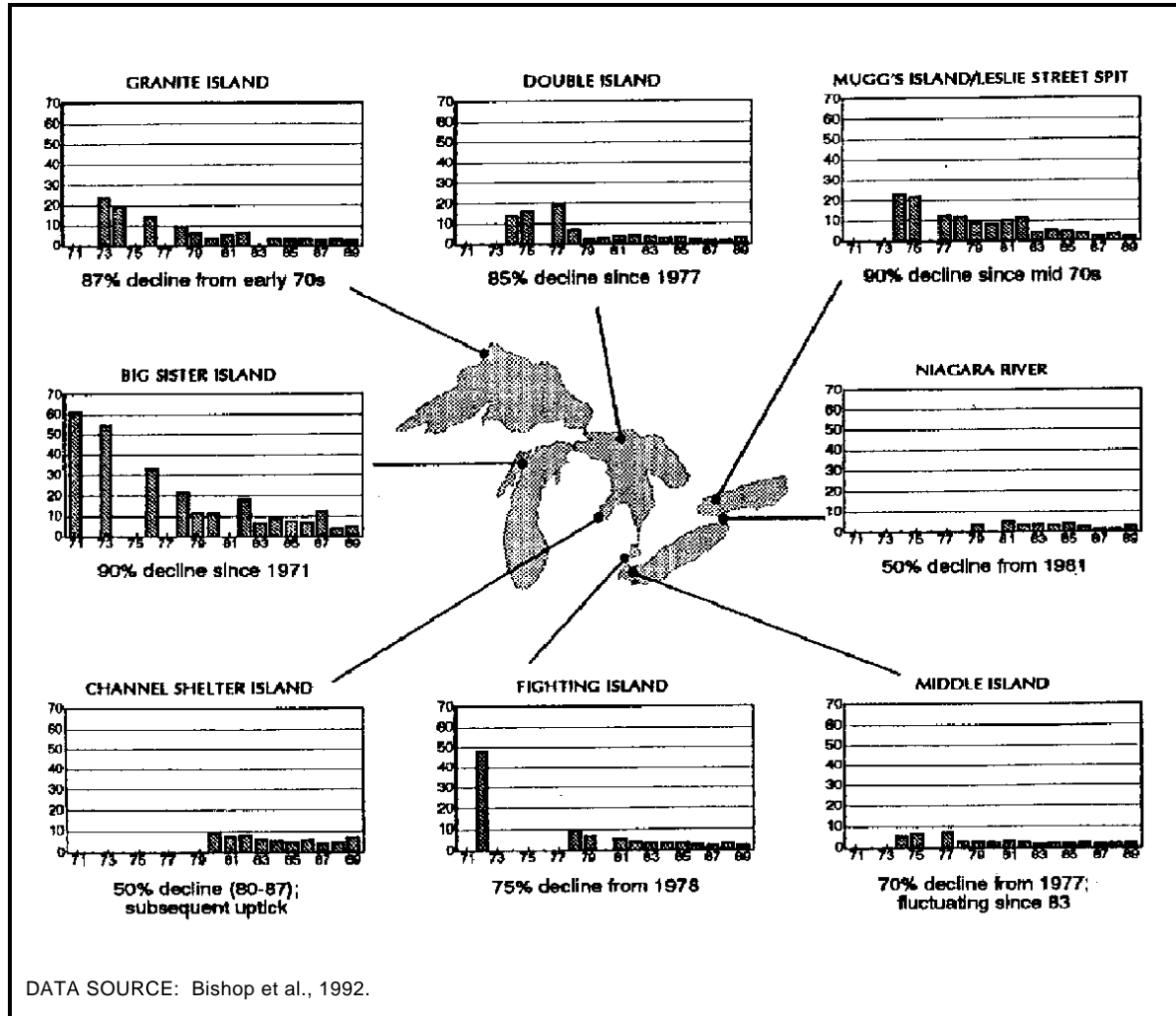


Figure 4-14b. Concentrations of DDE in Herring Gull Eggs for the Great Lakes.

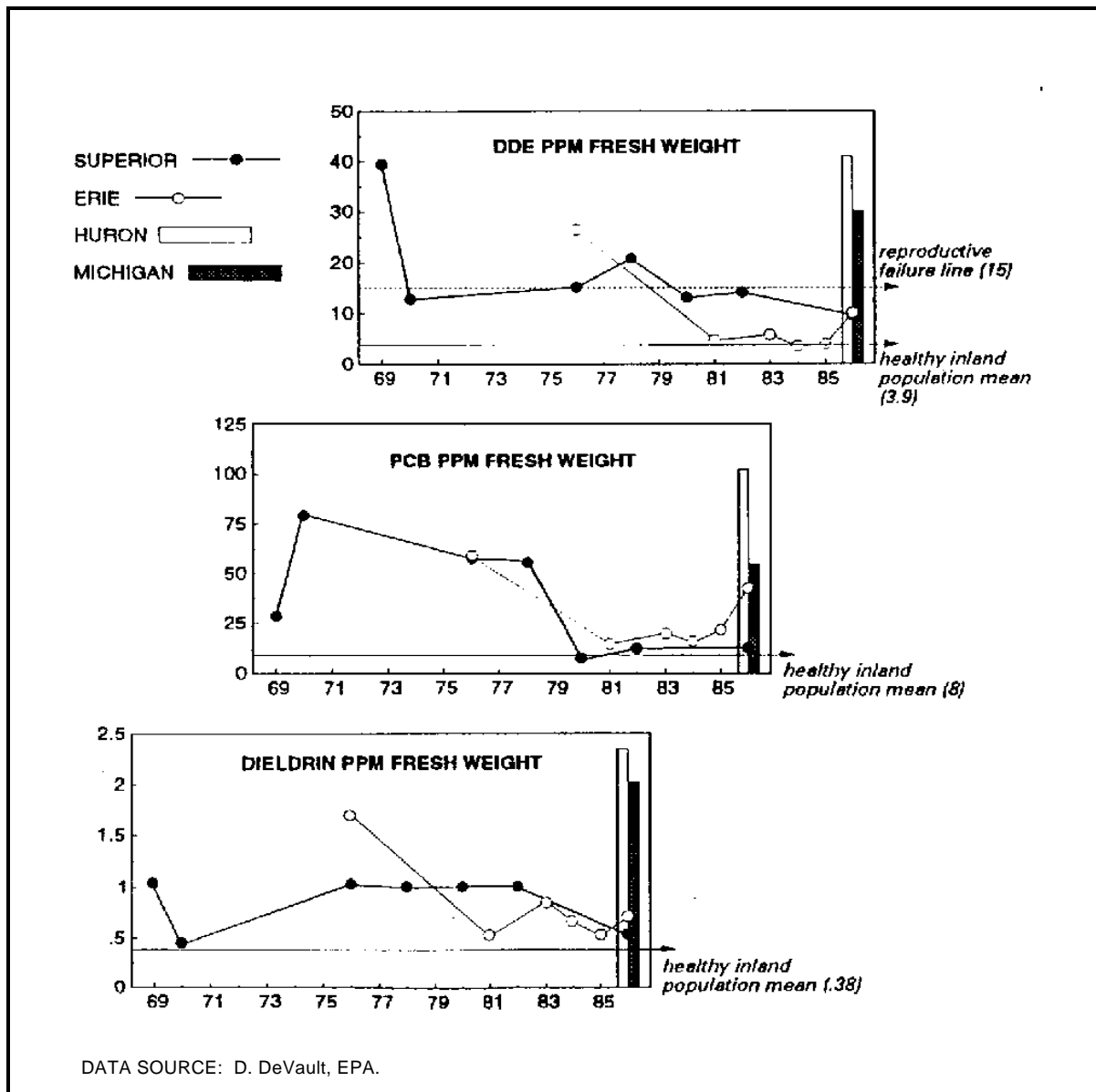


Figure 4-14c. Concentrations of DDE in Bald Eagle Eggs for the Great Lakes.

Mussels – DDT and its metabolites have been measured in mussels at a total of 21 U.S. locations around the Great Lakes (Except Lake Superior) as part of the NOAA Mussel Watch Program since 1992 (Robertson and Lauenstein, 1998). No trend information is available since most locations have only been sampled once during this period, however, some interesting findings related to DDT were observed. DDT was the only organo-chlorine (OC) pesticide to be detected in samples collected from all 21 sites. In addition, the highest OC pesticide concentrations were observed for total DDTs with the highest concentrations found in the southern basin of Lake Michigan. Concentrations greater than 160 ng/g (dry wt.) were observed in all samples collected from Milwaukee, WI. to Muskegon Harbor (with the exception of one station at the southernmost tip of Lake Michigan). These concentrations were an order of magnitude higher than those detected at any of the other locations in any of the Lakes. The predominant compounds detected, however, were the metabolites 4,4'-DDE and 4,4'-DDD indicating that the source was most likely historical and significant breakdown has occurred. In addition, the parent DDT and metabolite ratios found in mussels at two locations near S. Haven were different than any of the other mussel watch collection sites possibly indicating a source unique to this area.

Evidence of more recent DDT inputs, however, were found in both the St. Lawrence River and in east central Lake Erie, where the proportion of the parent DDT compound was upwards of 40% of the total DDTs measured, whereas at all other locations the proportion of DDT was less than 20%. The use of Dicofol, a registered pesticide containing DDT as an impurity, may be the source (Robertson and Lauenstein, 1998).

4.2.5 Toxaphene

4.2.5.1 Sources of Toxaphene to the Great Lakes

Toxaphene was primarily applied to cotton crops in the Southern U.S. for pest control. It was also used in the Great Lakes Region for control of unwanted fish stocks in small inland lakes (Swackhamer et al., 1998). Although historical inputs appear to have a non-atmospheric component, recent analysis of sediment cores in Lakes Superior and Ontario indicate that the dominant source of toxaphene to these lakes is through the atmosphere (Pearson, et al., 1997a). There is a possible non-atmospheric source in Northern Lake Michigan based on the results of a single sediment core taken from that area (Pearson, et al., 1997a). The non-atmospheric source of toxaphene to northern Lake Michigan has not been identified, though it could be from the Fox River. However, in 1997 a number of tributaries were sampled at locations that were felt most promising based upon past pesticide use and current industrial activity. Although final data have not been published, preliminary information indicates that non-atmospheric sources of toxaphene were not found (personal communication, EPA Region V). Both international and domestic sources may contribute to the atmospheric levels of toxaphene over the Great Lakes. Within the United States, sources may include toxaphene-contaminated sites outside the Great Lakes region.

4.2.5.2 Transport and Fate of Toxaphene in the Great Lakes

Atmosphere – Concentrations of toxaphene in the airshed of the Great lakes are summarized in Hoff, et al., (1992a). Other unpublished data were presented and discussed at a workshop on toxaphene in the Great Lakes held in Windsor Ontario in March 1996 (Eisenreich, 1996). The data presented indicated that toxaphene concentrations in air were about 30-50 pg/m³ in samples collected from 1989 to 1990 and ranged from approximately 2-12 pg/m³ in samples collected from 1992-1996 using a somewhat different quantification protocol. The toxaphene measured was predominantly in the apparent gas phase (>90 percent) and exhibited a relatively strong seasonal variation with summer concentrations approximately 4 times higher than winter concentrations (Hoff, et al., 1992a). There was little geographic variation over the Great Lakes. At the time of this report, there is concern over potential toxaphene emissions resulting from remediation of spoils and sediments at contaminated sites in Brunswick, Georgia. EPA is currently investigating the extent and impact of emissions from this source.

Surface Water – Published data on toxaphene concentrations in water were very limited in the Great Lakes prior to 1992. Measurements made since then are discussed in a recent publication (Swackhamer et al., 1998). Dissolved and particulate concentrations of toxaphene measured in 1994 through 1996 are presented in Table 4-7 (Swackhamer et al., 1998). The highest concentrations were detected in Lake Superior. Concentrations in the Great Lakes overall decreased from West to East. Recent data being collected from around the world show concentrations of toxaphene ranging from 0.03 ng/L in the Bering Sea, to approximately 0.25 in the Yukon River (Table 4-8). It is interesting to note that with the exception of Lake Superior, concentrations of toxaphene in the Great Lakes are similar to other recently reported data. Concentrations measured in Lake Superior are higher than would be expected based on data collected elsewhere.

Table 4-7. Water Concentrations of Toxaphene in the Great Lakes.

Lake	Dissolved Concentration (ng/L)	Particulate Concentration (ng/L) ^b
Lake Superior	0.29 (±0.04) ^b - 1.12 (±0.18) ^a	N/A
Lake Michigan	0.13 (±0.05) ^b - 0.38 (±0.12) ^a	0.017
Lake Huron	0.16 (±0.07) ^b - 0.47 (±.25) ^a	0.0054
Lake Erie	0.079 (±0.02) ^b - 0.23 (±0.007) ^a	0.0072
Lake Ontario	0.061 (±0.022) ^b - 0.17 (±0.07) ^a	0.0075

^a Source: Swackhamer et al. 1998

^b Source: Eisenreich, 1996

Table 4-8. Global Water Concentrations of Toxaphene.

Location	Toxaphene Concentration (ng/L)
Lake Baikal	0.064
High Arctic (below polar ice cap)	0.1
Bering/Chukchi Seas	0.03
Yukon River	0.02-0.25
Resolute Bay	0.03-.12
Amituk Lake (Canadian Arctic)	0.14

Source: Eisenreich, 1996

Soils/Sediment – Historical concentrations of toxaphene in sediments from the Great Lakes were measured in sediment cores in two studies which reported sediment concentrations with depth and accumulation rates for Lake Ontario, Lake Superior, and Lake Michigan (Howdeshell and Hites, 1996; Pearson et al., 1997a). Table 4-9 shows average concentrations found in surficial sediments and the maximum concentration reported in subsurface sediments. The first detection of toxaphene generally corresponds to sediments deposited between 1940 and 1950. The historical profiles of toxaphene observed in sediment cores from Lake Ontario clearly demonstrate that inputs to the Lake from the atmosphere and the Niagara River have declined since the mid-1970s. However, in Lake Superior and northern Lake Michigan, the data pertaining to decreases in sediment accumulation rates over the last 10 years are much less certain. For example, the maximum concentrations occur in the early 1970s to early 1980s in cores from all of the lakes. Surficial concentrations in most cores were similar at 15 ±4 ppb. The exception was one core collected from the northernmost portion of Lake Michigan where surficial concentrations were upwards of 40 ppb. Figure 4-15 shows the profiles of the cores collected in the three lakes.

Further examination of the sediment core data appears to indicate that toxaphene was detected in many of these cores prior to its production in 1946. However, it is unlikely that other sources of toxaphene were present prior to its introduction as a pesticide in the later 1940's. The authors could not explain the extremely early onset dates in two of the Lake Michigan cores but did see similar results for other chlorinated organics in these cores, suggesting that the results may be an artifact of sampling. In addition, there is some uncertainty associated with age dating sediment cores.

Table 4-9. Toxaphene Surficial and Subsurface Maxima Sediment Concentrations from Lakes Superior, Michigan and Ontario.

Lake	Surficial Concentration (ppb)	Subsurface maximum concentration (ppb)
Superior	12-15	19-29
Michigan - southern basin	15-22	20-28
Michigan - northern basin	32-45	40-48
Ontario	14-16	24-42

Data regarding current levels of toxaphene in soils in the vicinity of the Great Lakes were not available. Toxaphene has historically been detected in urban and agricultural soils throughout the United States (USDHHS, 1994a). Concentrations as high as 52.7 ppm were reported in surface soils in 1969. More recently, however, toxaphene was not detected in confined disposal facilities in the Great Lakes Region (USDHHS, 1994b).

4.2.5.3

Trends in Birds

Concentrations
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One study
al., 1997) has
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(Figure 4-22).
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1990. Only trace amounts (0.5 ppm) were observed in fish from Lake Ontario (DeVault *et al.*, 1996).

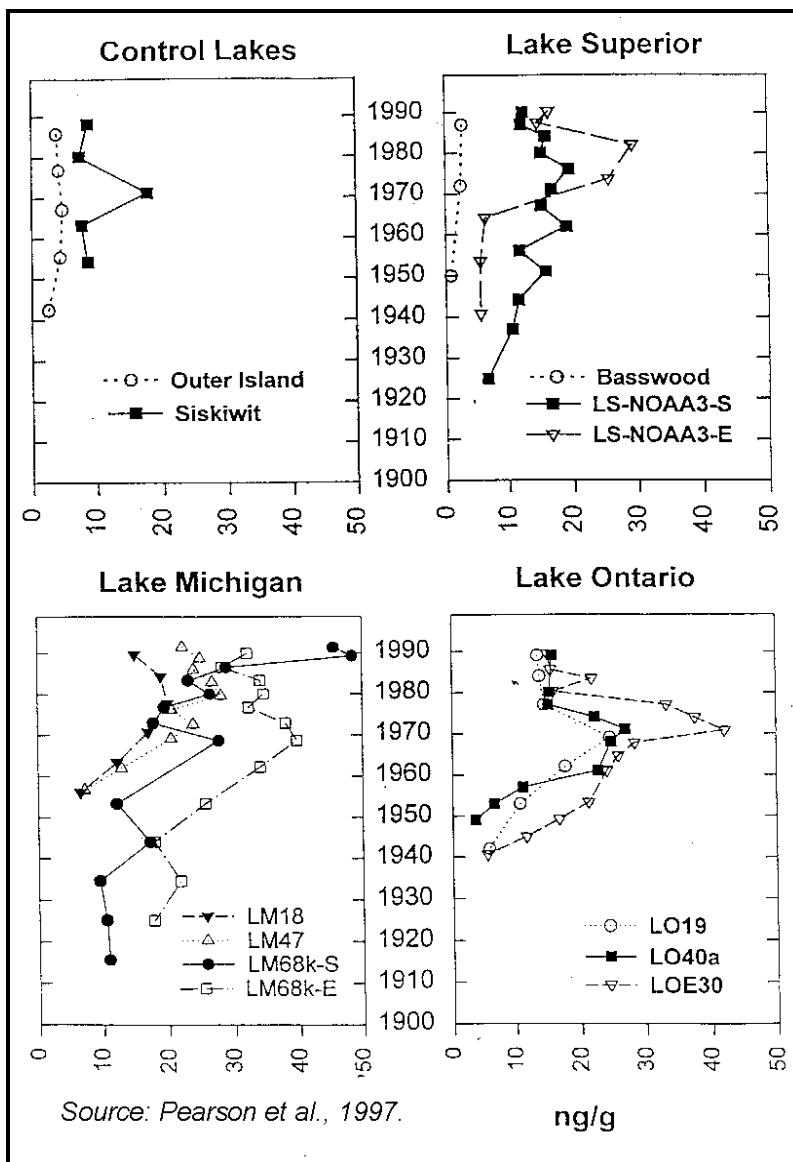


Figure 4-15. Sediment Toxaphene Profiles.

Toxaphene Fish and

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have not been
enough to fully
possible trends.
(Glassmeyer, *et*
reported a
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(normalized to
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and reports no
change in fish
Superior for the
period

However, these
are based on
only from 1982
Additional data
study (DeVault
indicate that
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virtually eliminated when they are no longer detected in any of the environmental compartments of the Great Lakes. The persistent nature of these compounds, that trait which rendered them so problematic, makes the prospect of virtually eliminating them from all environmental compartments difficult. Cortes et al. (1998) discussed the concept of virtual elimination in terms of atmospheric concentrations and estimated dates when this “virtual elimination” might be expected. Figure 4-17 illustrates the predicted dates for various locations around the Great Lakes where significant reductions in some of the Level I pesticides have been observed. Note that the term “virtual elimination” in this study was defined as “not detected at or below the current state of the art detection limits” (instrument response of 0.1 pg/m³). As technology and methodologies improve, detection limits will go down, extending the time required to achieve virtual elimination under this definition.

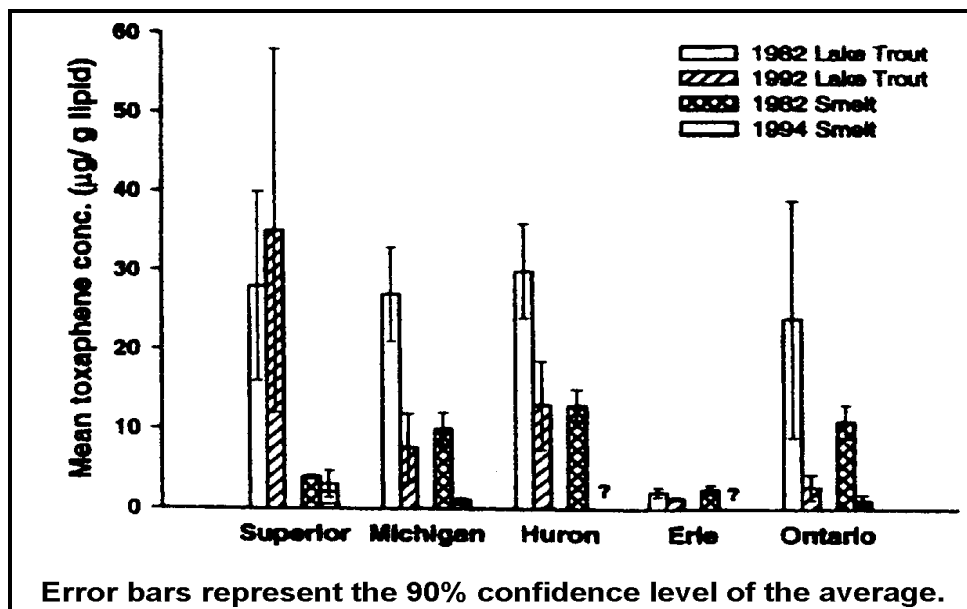


Figure 4-16. Mean Concentration of Toxaphene (lipid normalized) in Lake Trout, Walleye, and Smelt in the Great Lakes in 1982 and 1992/1994.

4.2.6 Elimin

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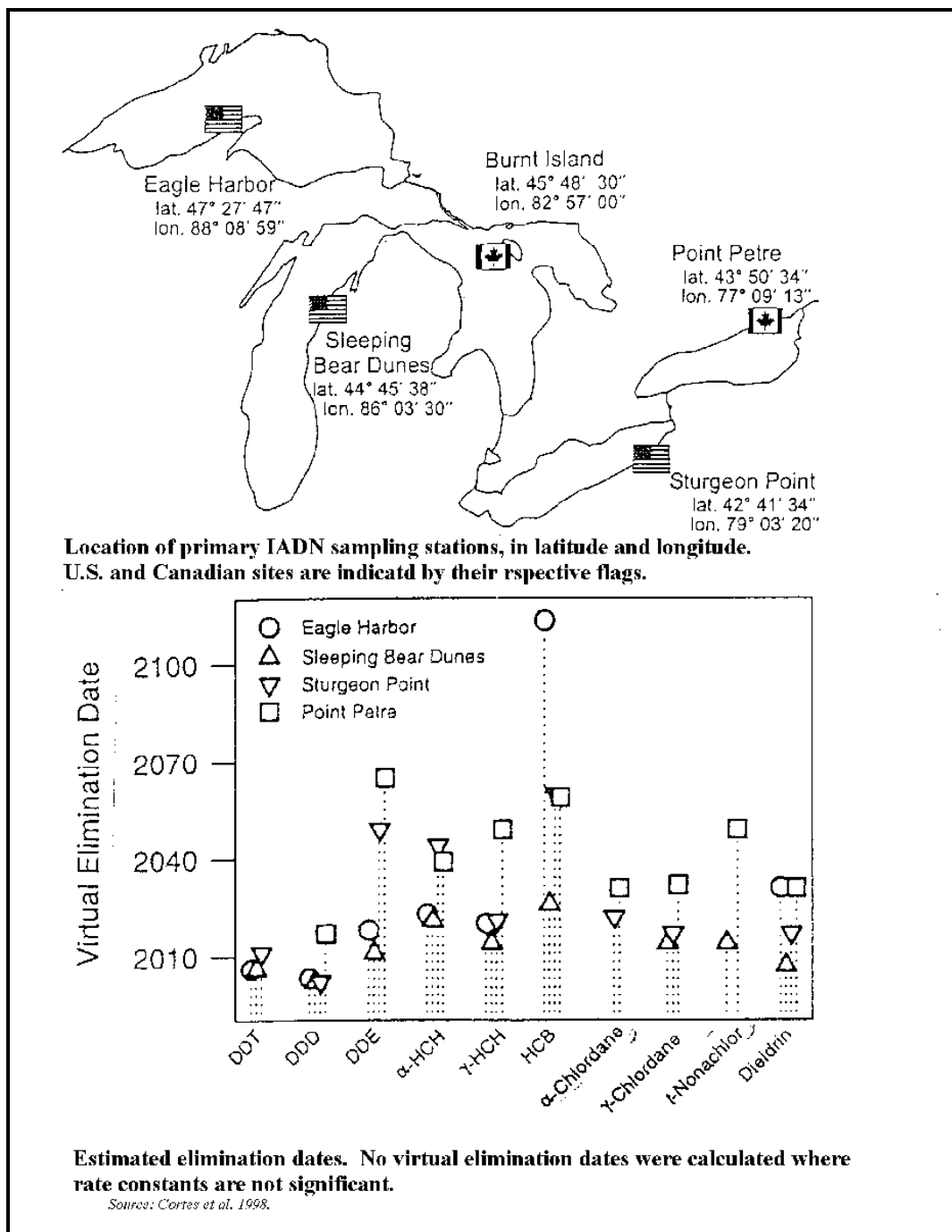


Figure 4-17. Virtual Atmosphere Elimination Dates.